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Technical Report Series

Water and Sediment Quality Assessment of Peninsula Harbour, Lake Superior - Spring 1984 and 1985



NORTH SHORE
OF LAKE SUPERIOR
REMEDIAL ACTION PLANS

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**WATER AND SEDIMENT QUALITY ASSESSMENT OF
PENINSULA HARBOUR, LAKE SUPERIOR -
SPRING 1984 AND 1985**

by

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October 1990

ISBN 0-7729-7502-7 (2 v. set)

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ACKNOWLEDGEMENTS

The authors would like to acknowledge the efforts of C. Cherwinsky who planned and coordinated the 1984 field work for this report.

The authors would like to thank D. Kennedy for data retrieval and editing, and M. Walsh and K. Somers for helpful advice on the statistical analyses.

The report was reviewed by D. Boyd, K. Sherman and M. Walsh of the Great Lakes Section, Water Resources Branch; and A. Laine, Water Resources Assessment, Technical Support, Northwestern Region. Their comments are appreciated.

This study was funded, in part, by Environment Canada under the terms of the Canada-Ontario Agreement on Great Lakes Water Quality.

FOREWORD

The results of this study formed part of Ontario's contribution to the Lake Superior Intensive Surveillance and Monitoring Program, and the 1986 Lake Superior Task Force Plan (Appendix "B").

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EXECUTIVE SUMMARY

Survey Design

The Peninsula Harbour area has been identified by the International Joint Commission as one of four Areas of Concern on the north shore of Lake Superior. The only point source dischargers to the area are the James River - Marathon Limited pulp and paper mill and the Marathon Water Pollution Control Plant (WPCP). Both the mill and the WPCP discharge their effluents into open Lake Superior, adjacent to Peninsula Harbour. A chlor-alkali plant was operated in the harbour area until 1977.

Environmental concerns established from previous studies included: a) mercury contamination from the former chlor-alkali plant, resulting in accumulation in fish and sediments; b) PCB contamination in the sediments of the harbour and open Lake Superior; c) bacteriological contamination from the mill and WPCP; and d) aesthetic impairment from the unsightly foam mats produced by the mill effluent.

Secondary treatment was installed at the WPCP in 1982. In September, 1984 the pulp and paper mill installed a submerged diffuser outfall for its effluent. Water quality studies were conducted in May of 1984 and 1985 to determine if there was any significant difference in the areal extent and concentration of selected water quality parameters in the receiving environment following this change in discharge. Surficial sediment studies were also conducted in 1984 only. Samples of the mill intake and effluent, and the WPCP effluent, were collected in both years. Additional objectives of the water, sediment and effluent surveys were to: a) update baseline data in these areas; b) assess the extent of the impairment of the mill and WPCP effluent to the receiving water and sediment quality; and c) link offshore sediment contaminants to point sources.

Water quality sampling was conducted in Peninsula Harbour and Lake Superior at 62 stations in 1984 and at 52 stations in 1985. Water and effluent samples were analyzed for physical parameters, inorganics, metals, nutrients, microbiological organisms, resin/fatty/aromatic acids, organohalide compounds, organochlorine pesticides, and chlorinated and speciated phenolics. Sediment samples were collected at 42 stations, and analyzed for physical parameters, inorganics, metals, organochlorine pesticides, and chlorinated and speciated phenolics. Depth profiles of conductivity, water temperature and dissolved oxygen (1984 only) were measured at several stations in both years. Intensive profiles over the diffuser were conducted in 1985. The profile samples were analyzed for most of the parameters analyzed in the water samples to provide information on initial mixing.

Effluent Results

The effluent quality of the Marathon WPCP was significantly improved after the installation of secondary treatment. Total coliform counts in both 1984 and 1985 were substantially reduced from those reported in 1978. Apparent colour, nitrate and total phosphorous decreased significantly from May, 1984 to May, 1985. A significant increase in chloride concentrations probably reflected more intensive disinfection practices at the plant. The effluent was well below the general Ontario Ministry of the Environment (OMOE) effluent requirements for 5-day Biochemical Oxygen Demand (BOD₅) and Total Suspended Solids (TSS) of 25 mg/L for plants with secondary treatment. Levels were less than 3.0 mg/L of BOD₅ and less than 4.0 mg/L of TSS in both 1984 and 1985. Total phosphorous concentrations slightly exceeded the Great Lakes Water Quality Agreement value for the Upper Great Lakes of 1.0 mg/L in both years, with mean values of 3.5 mg/L and 1.5 mg/L

in 1984 and 1985 respectively. Given the oligotrophic nature of the receiving water, these levels are probably not of concern.

The James River - Marathon Limited pulp and paper mill effluent was below the control order limit for discharge of suspended solids in both 1984 and 1985. Total dissolved solids and total solids decreased significantly during this time, although there was a concurrent increase in turbidity. The mill slightly exceeded the control order limit for BOD₅ loadings on May 16, 1984, probably because of reduced production on this day. Samples collected on May 20, and monthly and yearly average loadings were within this limit. The mill was within the regulatory limit for BOD₅ on all occasions in 1985.

Sodium concentrations decreased significantly from a mean value of 380 mg/L in 1984 to a mean value of 321 mg/L in 1985. Chemical oxygen demand (COD) increased significantly between the two years. Metals concentrations were generally low, and remained constant between years, with the exception of a significant increase in lead. Although there was no statistically significant change in mercury, concentrations were reduced from a mean value of 1.59 mg/L in 1984 to 0.08 mg/L in 1985. Total phosphorous concentrations were less than 0.5 mg/L in both years.

Microbiological counts were, with the exception of low numbers of heterotrophic bacteria, below detection level. The low fecal coliform count indicates that *Klebsiella pneumoniae* contamination is not a problem with this mill.

Three resin acids (dehydroabietic acid, pimaric acid and isopimaric acid) decreased significantly from 1984 to 1985. This may be due to the use of hardwoods and softwoods as furnish during the 1985 sampling, as opposed to solely softwoods during the 1984 sampling. Three of the fatty acids (palmitic acid, stearic acid and linoleic acid) also decreased significantly. Two phenolic compounds, vanillin and 2,4,6-trichlorophenol, decreased significantly. Total reactive phenolics in the effluent were greater than 2000 µg/L in both years. Despite this apparent decrease in the concentration of toxic components, the mill effluent continues to be highly toxic to fish. In 1986, the rainbow trout 96 hour LC₅₀ was 12 - 15%. The high toxicity implies that the observed decrease in toxic components is a temporary phenomenon associated with hardwood runs.

The parameters exhibiting significant differences in concentration between years in the mill effluent and intake water are completely exclusive, indicating that the changes noted in the mill effluent quality are primarily attributable to process and treatment changes in the mill.

Water Quality Results

The depth profiles conducted at the stations within the harbour and in open Lake Superior showed relative uniformity of conductivity, water temperature and dissolved oxygen (1984 only) from the surface to the bottom. These results indicate a well-mixed water column. Stations near the mill outfall showed minor variations in conductivity and water temperature throughout the water column in both years. Profiles of these stations illustrated the difference between 1984 surface discharge and 1985 bottom discharge.

Most parameters exhibited a distinct dilution profile above the submerged diffuser outfall. Concentrations at the diffuser tended to decrease from the first to the last port. Differences in the profiles for total reactive phenolics at two different time periods in the same day again reflect the strong influence of wind speed and direction on the effluent plume and subsequent dilution.

Conductivity (25°C), total dissolved solids, total suspended solids, sodium, ammonia, BOD₅, COD and total reactive phenolics decreased significantly from 1984 to 1985. These parameters are associated with both the mill and WPCP effluents. These improvements may be attributed to improvement in effluent quality and increased dilution of the effluent resulting from the installation of the submerged diffuser discharge.

Water temperature, turbidity, iron and nitrate increased significantly from 1984 to 1985. Significant station differences were found for turbidity, sodium, chloride, BOD₅ and total reactive phenolics, indicating a definitive point source for these parameters.

Dissolved and suspended solids were shown to have decreased considerably from those recorded in previous surveys, and no longer appear to be a problem in the receiving water. Metals concentrations in water samples were generally low, with some samples exceeding the Ontario Provincial Water Quality Objectives (PWQO's) by a moderate amount.

The concentrations of ammonia, total Kjeldahl nitrogen (TKN), nitrite and nitrate did not exceed any water quality objectives, and were generally similar to background levels. Total phosphorous exceeded the PWQO for avoidance of nuisance algal growth at one station in 1984 and at nine stations in 1985 (near the mill and WPCP outfalls).

Bacterial counts were considerably reduced from previous surveys, and well below the PWQO's for recreational use. Bacterial contamination would appear to no longer be a receiving water impairment in Peninsula Harbour or open Lake Superior.

High, localized biochemical and chemical oxygen demands associated with the waters near the mill outfall were not evident in 1985 after the instalment of the submerged diffuser outfall. Dissolved oxygen concentrations in the study area were high (generally greater than 12 mg/L). This indicates that the oxygen demand from the effluents was not depleting oxygen in the receiving water environment during the sampling period.

The PWQO's for dehydroabietic acid and total resin acids were exceeded at one station below the mill and WPCP outfalls in 1985 only. Fatty acids were also only detected on this occasion.

Most volatile organohalide compounds analyzed were not detected. Chloroform, carbon tetrachloride, trihalomethanes and 2,3,6-trichlorotoluene (1985 only) were detected at a limited number of stations. Of the organochlorine pesticides, only α -BHC, γ -BHC (lindane) and aldrin were detected at low levels. These compounds are regularly detected at low concentrations throughout the Great Lake basin.

Although the PWQO for total reactive phenolics was exceeded frequently in both years, there have been no reports of fish tainting in this area.

No chlorophenolic compounds were detected in receiving waters. Of the speciated phenolics, the compounds phenol, homovanillic acid and acetovanillon were detected in 1985 only. Vanillin and guaiacol were detected in both years, but more frequently in 1985. The increased detection in 1985 is probably due to a change in laboratory method sensitivity and reporting units for these compounds.

Sediment Quality Results

The dynamic nearshore environment was characterized by sandy, coarse sediment. The finer sediments were found in the deeper depositional environments offshore.

Chromium and iron concentrations were above the sediment Open Water Disposal Guidelines (OWDG's) in most samples, while copper and iron concentrations only occasionally exceeded the guidelines. Mercury concentrations exceeded the OWDG at 52% of the stations. The highest concentration of 8.80 µg/g was found near the site of the former chlor-alkali plant in Jellicoe Cove. High concentrations were also found in the mouth of the harbour. Mercury concentrations were considerably reduced from those found in previous surveys. This reduction may be the result of the deposition of cleaner sediment over the contaminated locations and/or migration into deeper depositional areas. Grain-size corrected results for iron and copper suggest that the mill and WPCP may be significant sources of these metals, but that they are not being deposited near the outfalls because of the dynamic nature of the near-shore environment.

The organic content of the sediments, as measured by % Loss on Ignition (LOI) and Total Organic Carbon (TOC), was particularly high in Peninsula Harbour. This reflects the deposition of wood fibres and bark introduced by booming operations and surface runoff. Three stations exceeded the OWDG for % LOI in the harbour, with particularly high values in Jellicoe Cove.

Phosphorous concentration were generally low, with the OWDG being exceeded at only one station in open Lake Superior.

None of the chlorophenolic compounds analyzed were detected. The five speciated phenolic compounds detected in the water column were also found in the sediments in the harbour area. Only nine of the 21 organochlorine pesticides analyzed for were detected in at least one sediment sample.

PCB's were detected at 15 of the 35 stations where this compound was analyzed. Concentrations exceeded the OWDG at 12 of these stations. The persistence of this group of compounds is illustrated by the comparable levels (above 200 ng/g) found at the same station in Lake Superior in both 1984 and 1973.

Recommendations

1. Although sediment mercury concentrations are still above the open-water disposal guidelines, contamination is considerably reduced at the site of the former chlor-alkali discharge. This may be due to the deposition of cleaner sediments over the contaminated areas and/or migration and dispersion of the mercury from the original source into deeper depositional areas. Further assessment of sediment mercury should be conducted in depositional areas to determine the full areal extent of the contamination. Sediment cores should be collected in the areas of maximum concentration in Jellicoe Cove to determine the historical extent of mercury deposition. In addition, methylated mercury analyses should be done on both water and sediment samples from these areas to assess the bioavailability of the mercury to aquatic fauna.
2. PCB sediment contamination should be monitored on a regular basis to determine if the concentrations and areal extent of the contamination are changing over time. PCB concentrations should also be determined concurrently in the mill and WPCP effluent solids to determine if the contamination is due to current as well as historical deposition.
3. Based on the results of the surveys recommended in #1 and #2, options for remediation of contaminated sediments should be developed

4. As the quality of the effluent discharges and receiving water have improved since previous benthic invertebrate surveys, these surveys should be repeated to determine the effects of these changes on the macroinvertebrate populations and community structure.
5. The bioavailability and toxicity of contaminants in the sediment and water column should be determined through biomonitoring assessment procedures such as caged mussel and leech exposures, and sediment bioassays.
6. In view of recent concerns on organochlorine discharges from kraft pulp mills, further assessment should be made of these compounds and/or groups of compounds in the effluent, water, sediment and biota. Investigations into the presence of chlorinated dibenzo-p-dioxins and dibenzofurans are of particular concern.

1. INTRODUCTION

1.1 STUDY AREA

Peninsula Harbour is located on the northeastern shore of Lake Superior, approximately 290 kilometers east of the city of Thunder Bay. The harbour is sheltered by Hawkins Island in the west, the Peninsula to the south, and a hilly peninsula in the north extending out to Ypres Point. The study area included both Peninsula Harbour and the area immediately south of the Peninsula in Lake Superior (Figure 1).

1.2 BACKGROUND

The town of Marathon is the nearest populated center to the study area. The principle industry is the James River - Marathon Ltd. pulp and paper mill. This bleached kraft pulp mill was owned and operated by American Can of Canada prior to its sale in 1983. In 1985, the mill had an annual capacity of 150,000 tonnes, consisting of 36,000 tonnes of bleached hardwood kraft pulp, 105,000 tonnes of fully bleached softwood kraft pulp, and 9,000 tonnes of unbleached softwood pulp. Peninsula Harbour is the source of process water for the mill.

The location of past and present discharges to the harbour resulting from mill activities are illustrated in Figure 2. Currently, the mill effluents are pumped uphill to flow down the other side of The Peninsula in an open channel, and then out to the lake. If there is an overflow from the main effluent sump, effluent can be discharged to Jellicoe Cove.

The harbour was historically used for storage of logs to be pulped. Log storage and discharges relating to the debarking of logs were discontinued in 1983 when the source of wood fibre was changed to residual wood chips purchased from local saw mills. The harbour was again used for building rafts of sawlogs for transportation to Thunder Bay in 1987 and 1988.

The Marathon water pollution control plant (WPCP) is located approximately 1.3 km south of the mill outfall, and discharges approximately 1,996 m³/day to Lake Superior. The WPCP was upgraded to include secondary treatment in 1982. The pulp and paper mill's sanitary sewer collection was completed and connected to the WPCP prior to the end of

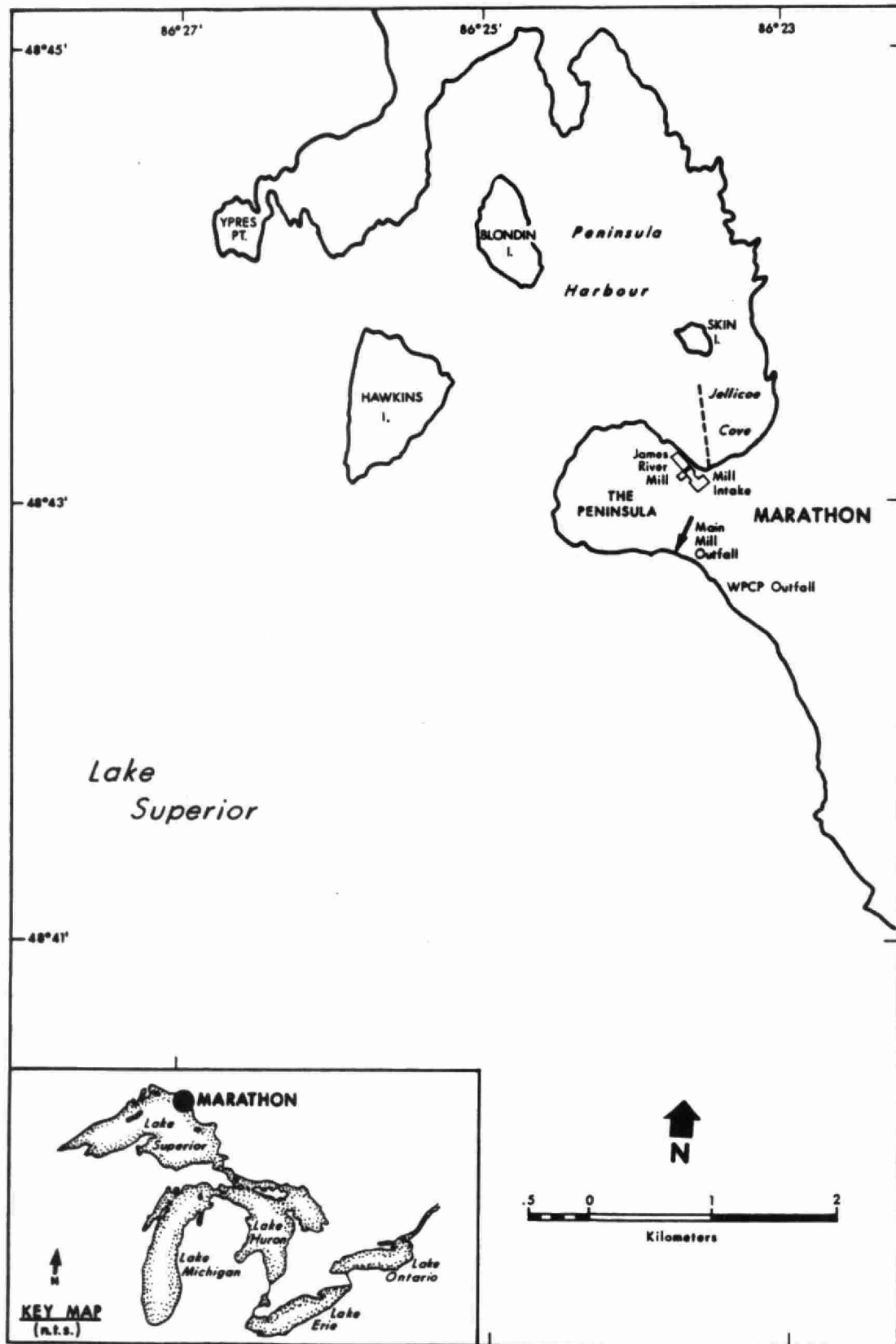
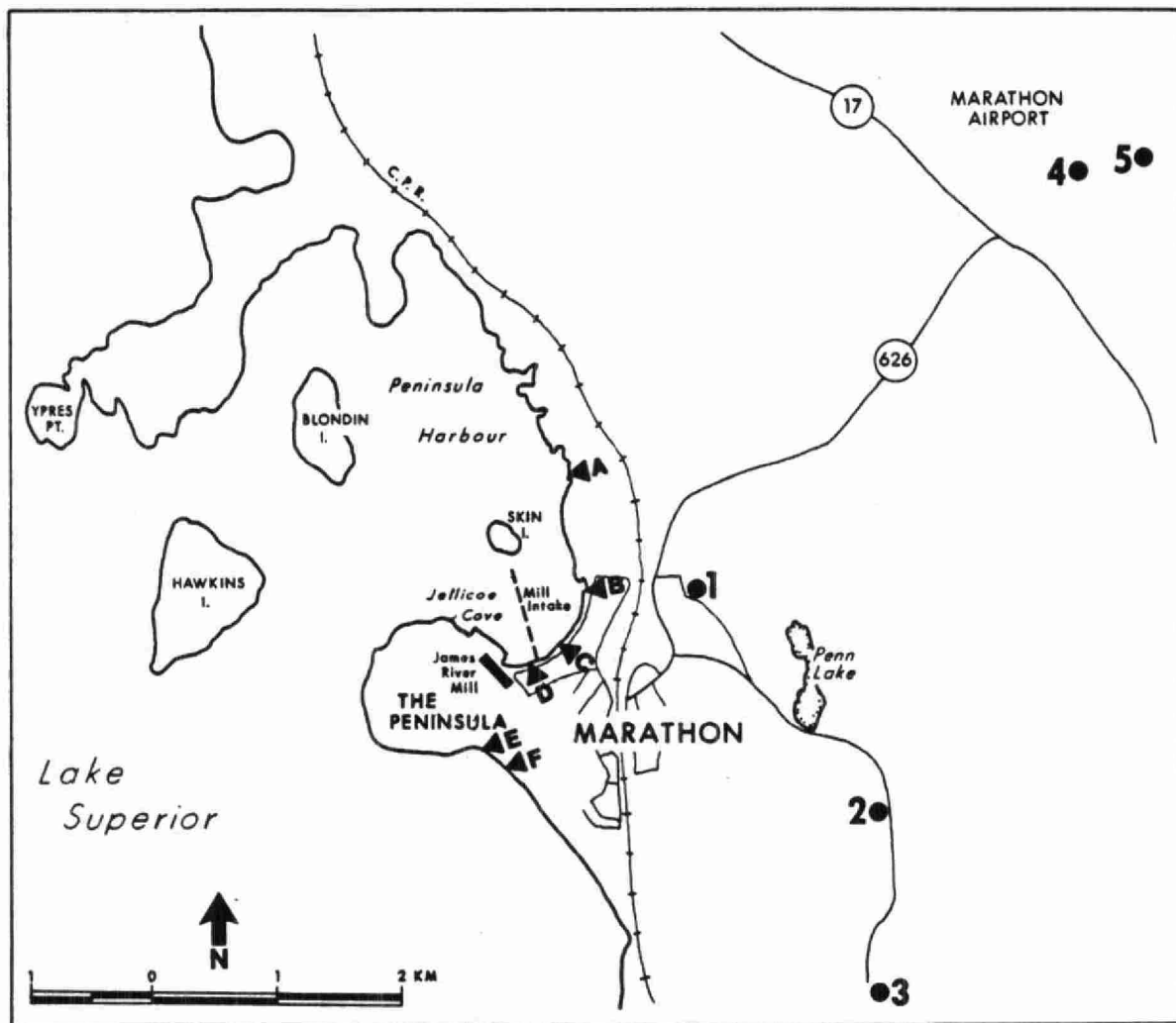


Figure 1. Location of Peninsula Harbour and the study area.



DISCHARGE LOCATIONS

- ◀A BARK POND OVERFLOW
- ◀B BARKER DRUM SHORE DRAIN
- ◀C WET DRUM BARKER OVERFLOW
- ◀D MILL SUMP OVERFLOW
- ◀E MAIN MILL OUTFALL (includes No.1 Bleachery Wastee)
- ◀F S.T.P. OUTFALL

WASTE DISPOSAL LOCATIONS

- 1 TOWNSHIP OF MARATHON - MUNICIPAL LANDFILL SITE
- 2 TOWNSHIP OF MARATHON - SLUDGE DISPOSAL SITE
- 3 JAMES RIVER - MARATHON LIMITED MERCURY DISPOSAL SITE
- 4 AMERICAN CAN OF CANADA LIMITED FORMER INDUSTRIAL WASTE DISPOSAL SITE (Closed)
- 5 JAMES RIVER - MARATHON LIMITED INDUSTRIAL WASTE DISPOSAL SITE

Figure 2. Waste disposal site locations and discharges to Lake Superior and Peninsula Harbour in the Marathon area.

1982, as per the requirements of an Ontario Ministry of the Environment (OMOE) Control Order.

In the past, a chlor-alkali plant was operated beside the kraft mill to manufacture chlorine, caustic soda, sodium hypochlorite, and sodium chlorate for use in the mill's pulping process. Chlorine and caustic soda, the primary products, were produced by the electrolysis of brine in electrolytic cells featuring graphite anodes and mobile mercury cathodes. During the lifetime of this operation, mercury was lost due to spills, leaks and vapour loss. Elevated mercury levels in the harbour sediments became of concern. Investigations conducted in 1975 and 1976 found levels as high as 112 µg/g at the outfall in Jellicoe Cove, with diminishing concentrations from the outfall. All lake trout captured in Peninsula Harbour during this time contained mercury concentrations in excess of the provincial guideline for consumption of 0.5 µg/g, with 38% of these fish above 1.0 µg/g.

As a result of these environmental concerns, the chlor-alkali plant was closed in 1977. A treatment process was designed and intalled to remove traces of mercury from the effluent stream. This process was in operation until 1984 when it was concluded that residual mercury in the effluent was no longer a concern. All mercury contaminated equipment was disposed of in a sealed compartment at an approved site.

Figure 2 shows the location of the mercury disposal site, and other existing and former municipal and industrial waste disposal sites. The industrial disposal site contains fly ash from the boilers, clarifier sludge, fibre, and lime mud waste.

Other historical environmental concerns related to the discharges from the pulp and paper mill include contamination of the sediments in the harbour and open Lake Superior with polychlorinated biphenyls (PCB's). Levels ranging from 10 to 250 µg/kg were found in the sediments in the study area in 1973 (Kinkead and Chatterjee 1974). The source of the PCB's was from leakage of transformer oil used in the pulp mill operations.

Bacterial contamination was another historical problem. Studies conducted in 1969 found that total coliforms, fecal coliforms and fecal streptococci greatly exceeded the Ontario Provincial Water Quality Objectives for swimming and bathing within 76 m of the main mill outfall in Lake Superior. The high bacterial contamination was attributed to the municipal and industrial wastewater discharges. High total coliform and fecal streptococci densities were also noted in Jellicoe Cove, reflecting the influences of the wastewaters from

the main sump overflow (OMOE 1972). A 1973 survey found that total coliforms, fecal coliforms and fecal streptococci showed elevated levels in Peninsula Harbour compared to control stations in non-industrialized nearshore areas in Lake Superior. While total and fecal coliform counts were within provincial guidelines, fecal streptococci counts exceeded these criteria at all stations (Kinkead and Chatterjee 1974).

For many years the mill effluent was characterized by unsightly thick brown foam mats. This floating debris carried materials that eventually settled to form objectionable colour and odour in the receiving water body. The dispersion of the plume was noted to be strongly governed by wind and current direction, and extended up to five km away from the main mill shore discharge. As a result, the mill was in violation of the general water quality criteria for recreational use and aesthetics. In September of 1984, James River Marathon Ltd. put into service a submerged ten-port diffuser discharge for the effluent as a remedial measure to eliminate foam from the surface of Lake Superior. The diffuser was also designed to provide sufficient initial dilution to ensure that the effluent would not be toxic to fish at the point of impingement with the lake surface.

Other operational and process changes made by the company during 1984 to improve environmental conditions were: the installation of a clarifier on selected waste streams; new filters to remove green liquor dregs before discharge to the sewer; the elimination of effluent from the debarking slasher operations; the installation of scrubbers on the lime kiln and tall oil reactor; and a new low odour recovery boiler with a large electrostatic precipitator.

1.2 OBJECTIVES

The objectives of this study were:

1. To provide a general update of the baseline data on: (a) effluent characterization for the James River Pulp and Paper mill and the Marathon Water Pollution Control Plant; and (b) water and sediment quality for the receiving environment in Peninsula Harbour and Lake Superior. These data will be used as input to the Remedial Action Plan (RAP) for the Peninsula Harbour Area, and the Municipal-Industrial Strategy for Abatement (MISA) program.
2. To assess the extent of the impairment of the mill and WPCP effluent to the receiving water and sediment quality.
3. To determine if there is any significant difference in the areal extent and concentration of selected water quality parameters in the receiving environment following the installation of a submerged 10 port diffuser discharge for the James River Marathon Pulp and Paper Company.
4. To link offshore sediment contaminants to point sources.

2. SURVEY DESCRIPTION AND METHODS

2.1 SURVEY DESCRIPTION

On May 16, 19 and 20, 1984 water samples were collected at 62 stations located in Peninsula Harbour and Lake Superior. On-shore samples were taken from the pulp and paper mill effluent, the WPCP effluent and the mill raw water intake. The 1984 station locations are illustrated in Figure 3. The water quality parameters determined for the samples are summarized in Table 1. The station selection grid was designed to assess the effects of the mill and WPCP discharges on the water quality of the harbour and Lake Superior. As previous studies had noted that the changeable wind and current direction resulted in a large areal impact from the mill's discharge plume, the study area was extensive.

A follow-up water quality survey was carried out on May 14 and 17, 1985 to determine if the installation of the diffuser discharge in September, 1984 had resulted in any significant difference in the concentrations and/or areal extent of the water quality parameters measured in 1984. Figure 4 and Table 1 show the 1985 station locations and sample parameters, respectively. Ten of the stations used in the 1984 survey were omitted from the 1985 survey on the basis that data from these stations were not necessary to update water quality information.

Replicate samples were collected from selected stations in the 1985 survey to determine the sampling and/or analytical variability within and between survey days. Successive replicate samples were collected at stations #368, #376, #383, #385, #393, #396, #407, #417, #418 and #426. These stations were selected to cover the range of concentrations from the mill effluent source (mill outfall station #393) to background conditions (open lake control station #426). The replicate samples were primarily used to qualitatively assess the validity of questionable data.

In 1985, the choice of parameters to be analyzed and the number of samples analyzed for each parameter was based on the volatility of the compound, and consideration of laboratory loads and costs. For example, fewer samples were collected for stable parameters (such as sodium) than for volatile parameters (such as reactive phenolics) because the variation in sodium analysis was expected to be low.

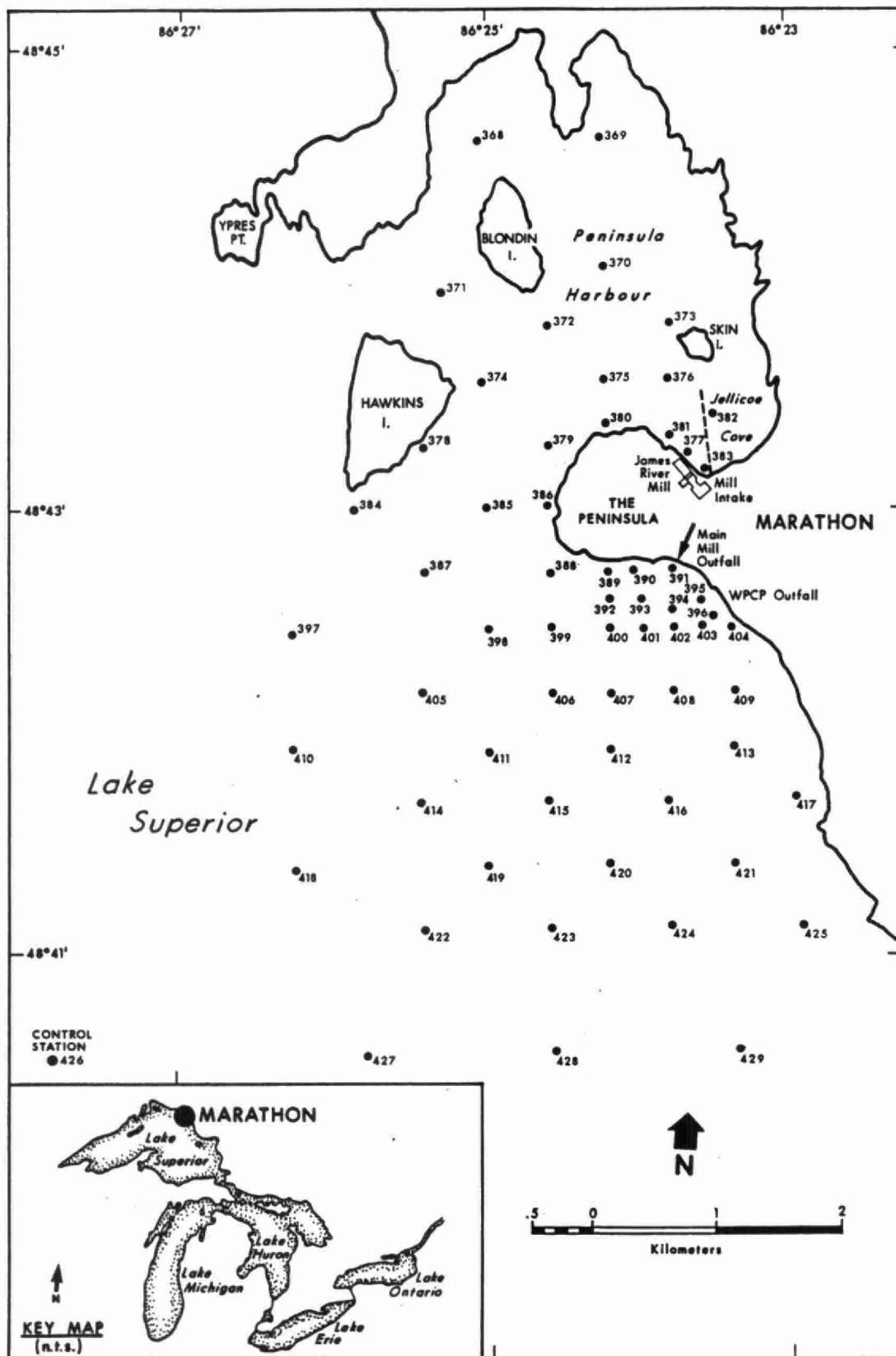


Figure 3. Sampling locations for the 1984 water quality survey.

Table 1. Parameters analyzed in water samples collected in Peninsula Harbour/Lake Superior in 1984 and 1985 (⁸⁴ 1984 only, ⁸⁵ 1985 only).

<u>Physical Parameters:</u>	<u>Resin Acids:</u>	<u>Chlorinated Phenolics:</u>
Colour (apparent)	Abietic Acid	2-chlorophenol
Colour (true) ⁸⁴	Dehydroabietic Acid	4-chlorophenol
Conductivity (ambient)	Isopimaric Acid	2,4-dichlorophenol
Conductivity (at 25°C)	Levopimaric Acid	2,3,4-trichlorophenol
Total Dissolved Solids (TDS)	Neoabietic Acid	2,4,5-trichlorophenol
Total Suspended Solids (TSS)	Palustric Acid	2,4,6-trichlorophenol
Total Solids (TS)	Pimaric Acid	2,3,4,5-tetrachlorophenol
Temperature	Sandaracopimaric Acid	2,3,5,6-tetrachlorophenol
Turbidity		2,4,5,6-tetrachlorophenol
	<u>Fatty Acids:</u>	Pentachlorophenol
<u>Inorganics:</u>	Arachidic Acid	Chloro-p-cresol
Chloride (reactive)	Capric Acid	
Cyanide (available) ⁸⁵	Lauric Acid	<u>Speciated Phenolics:</u>
Cyanide (free) ⁸⁴	Linoleic Acid	Phenol
pH	Myristic Acid	Vanillone
Sodium	Oleic Acid	Homovanillic Acid
Sulphate	Palmitic Acid	Guaiacol
	Stearic Acid	Syringaldehyde
		Acetovanillon
<u>Metals:</u>	<u>Aromatic Acids:</u>	Acetosyringone
Aluminum	Benzoic Acid	p-Cresol
Arsenic	Salicylic Acid	2,5-Xylenol
Barium	Phthalic Acid	
Cadmium		<u>Organochlorine Pesticides:</u>
Cobalt ⁸⁴	<u>Volatile Organohalides:</u>	Aldrin
Chromium ⁸⁴	Hexachlorobutadiene	α-BHC
Copper ⁸⁴	Chloroform	β-BHC
Iron	Carbon Tetrachloride ⁸⁴	γ-BHC
Lead	Octachlorostyrene	α-chlordane
Mercury	Trihalomethanes (total) ⁸⁵	γ-chlordane
Nickel ⁸⁴	Trichloroethylene ⁸⁴	Dieldrin
Selenium ⁸⁴	Tetrachloroethylene ⁸⁴	Methoxychlor
Silver ⁸⁴	Dichlorobromoethane	Endrin
Zinc	Chlorodibromoethane ⁸⁵	Endosulfan Sulphate
	Hexachloroethane	Endosulfan I
<u>Nutrients:</u>	2,3,6-trichlorotoluene	Endosulfan II
Ammonia	2,4,5-trichlorotoluene	Heptachlorepoxyde
Nitrate	2,6,A-trichlorotoluene	Heptachlor
Nitrite ⁸⁵	1,2,3-trichlorobenzene	Mirex
Total Kjeldahl Nitrogen (TKN)	1,2,4-trichlorobenzene	PCB (total)
Phosphorous (total)	1,3,5-trichlorobenzene	Oxychlordane
	1,2,3,4-tetrachlorobenzene	o,p'-DDT
<u>Microbiological:</u>	1,2,3,5-tetrachlorobenzene	p,p'-DDD
<i>Escherichia coli</i> ⁸⁴	1,2,4,5-tetrachlorobenzene	p,p'-DDE
Fecal coliforms ⁸⁴	Pentachlorobenzene	p,p'-DDT
Fecal <i>streptococci</i> ⁸⁴	Hexachlorobenzene	Dicamba ⁸⁴
Heterotrophic bacteria		Picloram ⁸⁴
<i>Pseudomonas aeruginosa</i> ⁸⁴		Silvex ⁸⁴
Total coliforms		2,4-D ⁸⁴
Total coliforms (background)		2,4-DB ⁸⁴
		2,4-DP ⁸⁴
<u>Organics:</u>		2,4,5-T ⁸⁴
Biochemical Oxygen Demand (BOD ₅)		
Chemical Oxygen Demand (COD)		
Dissolved Oxygen (DO)		
Dissolved Organic Carbon (DOC)		
Phenolics (total)		
Tannins		

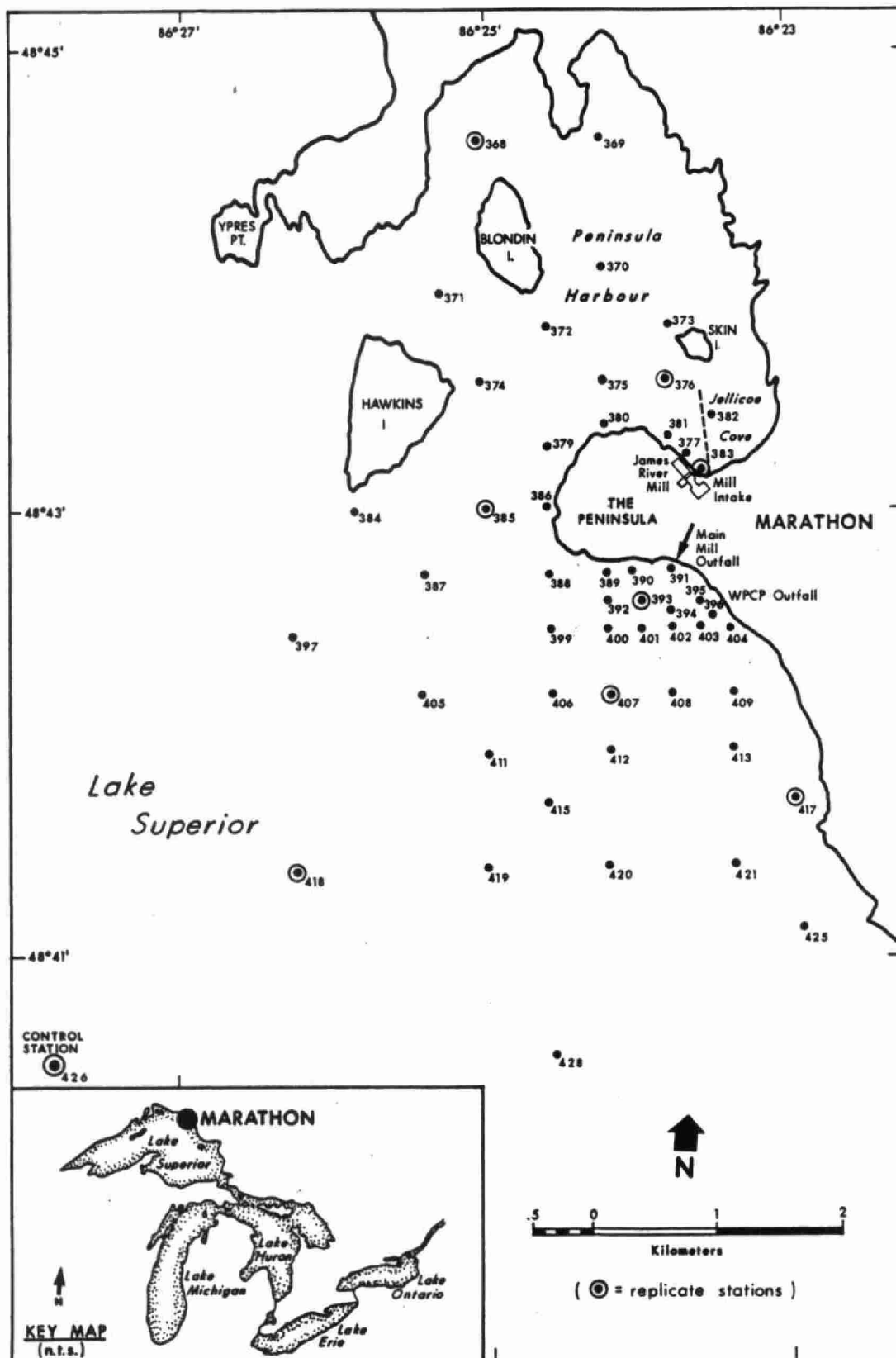


Figure 4. Sampling locations for the 1985 water quality survey.

The analysis of bacterial samples is restricted to a maximum shelf time of 48 hours, and samples are not analyzed on the weekends. The Victoria Day long weekend therefore restricted microbiological sample collection to May 14, 1985.

Pulp and paper mill and WPCP effluent samples were also collected in 1985 during the grid survey days to provide data for effluent characterization. The mill intake was also sampled as a control to be compared to the mill effluent samples. Samples were taken in both the morning and the afternoon at each on-shore location to improve the accuracy of the measurement and allow for better determination of variation.

Depth profiles of conductivity and water temperature were measured at several stations in both years. The stations and dates of sampling are summarized in Table 2. Dissolved oxygen profiling was also conducted in 1984. Equipment problems prohibited the planned measurement of dissolved oxygen in 1985. Depth profiles were taken 1.0 m below the surface, 0.5 m from the bottom and at appropriate intervening depths.

Additional intensive profiles over the diffuser were conducted on May 21, 1985. Samples were collected at the beginning, mid-point and end of the diffuser pipe. These samples were analyzed for most conventional water quality parameters to provide the data necessary to calculate initial mixing.

Plume tracking was conducted in 1985 only. Although ideally tracking should have been conducted concurrently with the diffuser profiling, equipment malfunctions on the survey vessel forced postponement until May 23. Drogues were released twice at the diffuser during the day. Mill effluent composite samples were also collected on both May 21 and 23.

Surficial sediment samples were collected in 1984 only. The samples were collected on May 14, 18, 24 and 25, 1984 at 42 selected stations (Figure 5). Due to adverse weather conditions, several days were required to collect samples at all stations. The parameter list is summarized in Table 3.

2.2 FIELD METHODS

Water quality sampling procedures were the same in both years of the survey. Stations were positioned by radar and depth sounding equipment. Samples to be analyzed for

Table 2. Depth profiling survey summary, 1984 and 1985.

Date	Stations Surveyed	Parameters Analyzed
1984		
May 16	#368 - 375 #392 - 428	Dissolved Oxygen, Conductivity and Water Temperature
May 19	#368 - 379 #381 - 381 #384 - 388 #391 #397 - 429	"
May 20	#387 - 388 #390 #391 - 395 #397 - 409	"
1985		
May 14	#396 #388 - 390 #393 - 394 #399 - 403 #407, #409 #413, #417 #426	Conductivity and Water Temperature
May 17	#394 #401 - 404 #408 - 409 #413, #417 #421, #425	"

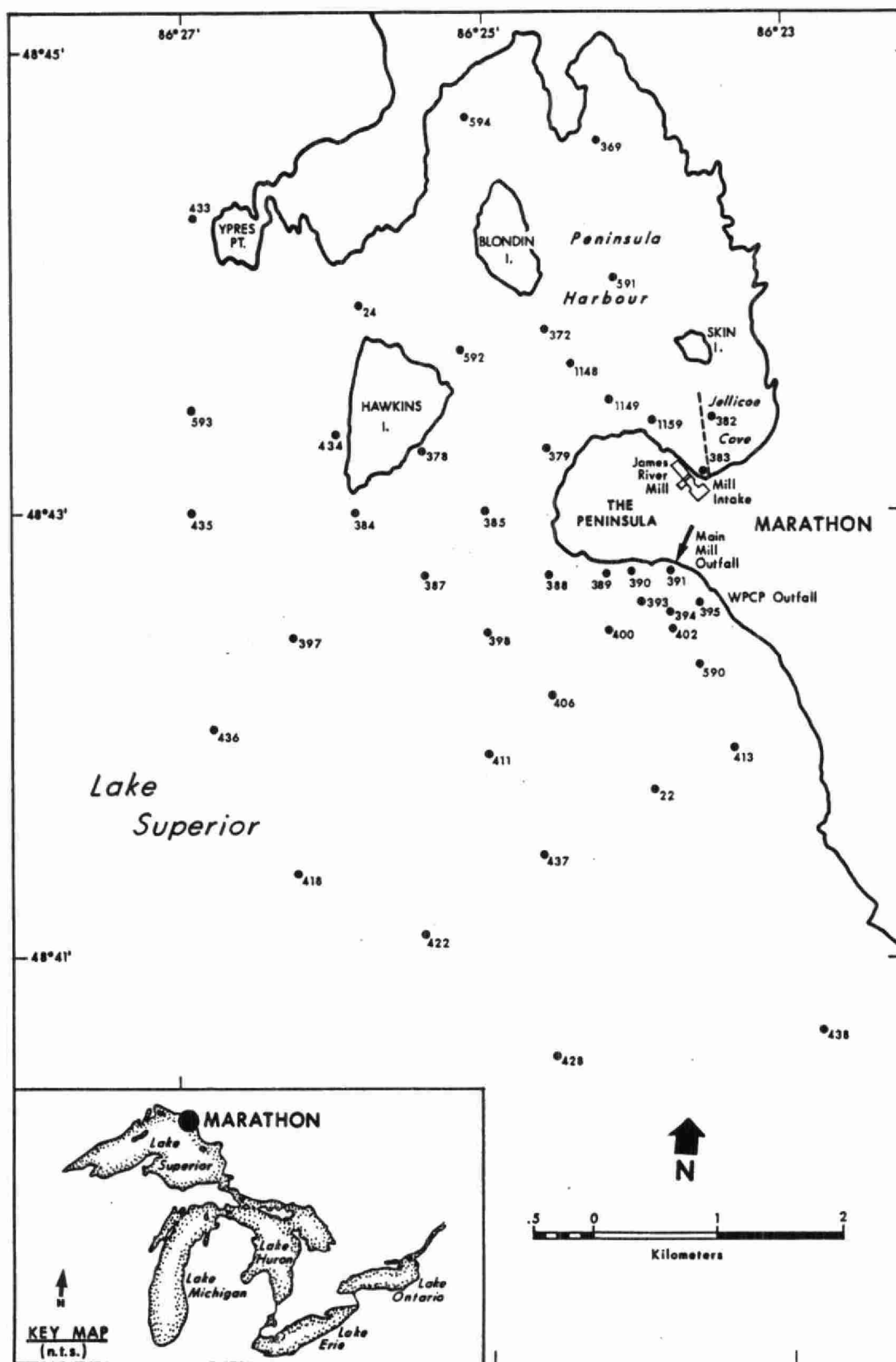


Figure 5. Sampling locations for the 1984 surficial sediment survey.

Table 3. Parameters analyzed in surficial sediment samples collected in Peninsula Harbour/Lake Superior in 1984.

Physical Parameters:

Particle size
Loss on ignition (%)

Inorganic Parameters:

pH
Phosphorous (total)
Sulphur (reducible)
Sulphur (total)

Metals:

Aluminum
Cadmium
Cobalt
Chromium
Copper
Iron
Mercury
Manganese
Nickel
Lead
Zinc

Organic Parameters:

Solvent Extractables
Total Organic Carbon (TOC)

Chlorinated Phenolics:

2-chlorophenol
4-chlorophenol
2,4-dichlorophenol
2,4,5-trichlorophenol
2,4,6-trichlorophenol
2,4,5,6-tetrachlorophenol
2,3,4,5-tetrachlorophenol
Pentachlorophenol
Chloro-p-cresol

Speciated Phenolics:

Phenol
Vanillone
Homovanillic Acid
Guaiacol
Syringaldehyde
Acetovanillon
Acetosyringone
p-cresol
2,5-xilenol

Organochlorine Pesticides:

Aldrin
 α -BHC
 β -BHC
 γ -BHC
 α -chlordane
 γ -chlordane
Dieldrin
Methoxychlor
Endrin
Endosulfan Sulphate
Endosulfan I
Endosulfan II
Heptachlorepoxyde
Hexachlorobenzene
Heptachlor
Mirex
Oxychlordane
PCB (total)
o,p'-DDT
p,p'-DDD
p,p'-DDE
p,p'-DDT

organic compounds, metals and microbiological parameters were collected by immersing the appropriate containers directly into the water using a bacteriological sampling pole. A Kemmerer sampler was used to collect samples to be analyzed for nutrients and physical parameters. All samples were collected at a depth of 0.5 meters, with the exception of profile stations. The sampling containers and preservatives used for each compound or group of compounds are summarized in the Ontario Ministry of the Environment (OMOE) guide to the collection and submission of samples for laboratory analysis (OMOE 1985a).

For all stations, water temperature and dissolved oxygen (D.O.) were determined on board using a YSI 54RC thermistor/D.O. probe. On-board conductivity and pH were measured using a Beckman Solubridge meter and an Orion 501 meter, respectively. Wind direction was recorded on all sampling days.

Each of the sediment samples collected in 1984 was a composite of three Shipek grab samples. A composite sample was prepared by sub-sampling the top 3 cm of each grab sample and combining the three sub-samples in a solvent and distilled water rinsed glass pan. Large objects such as rocks, twigs or clams were removed before the appropriate jars were filled and shipped to the laboratory for analysis.

2.3 LABORATORY METHODS

Water sample analyses were conducted in the OMOE Laboratories in accordance with prescribed analytical methods and policies (OMOE 1983). Samples to be analyzed for physical parameters (conductivity, turbidity, pH and colour), mercury and bacteria were transported from the sample site to the OMOE Thunder Bay Laboratory for analysis. Samples to be analyzed for all other parameters were transported and analyzed in the OMOE Toronto Laboratory. In 1985, all total reactive phenolics were analyzed in the OMOE portable laboratory located on-site at Marathon. All sediment samples were analyzed at the OMOE Laboratory in Toronto.

3. RESULTS AND DISCUSSION

3.1 EFFLUENT CHARACTERISTICS

A summary of the all WPCP effluent (Station #2), pulp and paper mill effluent (Station #19) and pulp and paper mill intake (Station #8) quality data is contained in Appendix A.

3.1.1 WPCP Effluent

Table 4 provides summary statistics (median, mean, standard deviation, and number of observations) for the WPCP effluent data collected in 1984 and 1985. To determine if there were significant differences between the effluent quality in May 1984 and May, 1985, t-test comparisons were made between years for all parameters for which there were sufficient number of observations. The results are summarized in Table 5.

The plant reduced the apparent colour of its effluent significantly from a mean value of 21.0 HZU in 1984 to 16.7 HZU in 1985. The values of all other physical parameters remained relatively unchanged between years. Reactive chloride concentrations increased significantly from 1984 to 1985, perhaps reflecting more intensive disinfection practices at the treatment plant.

Concentrations of aluminum, barium, iron and lead increased slightly from 1984 to 1985. However, these increases are not statistically significant at the 5% confidence level. Nitrate and total phosphorous concentrations decreased significantly, signifying improved reduction of nutrients in the treatment process at the plant.

Although the numbers of heterotrophic and total coliform bacteria appear to have increased dramatically from 1984 to 1985, the 1984 data are based on single sample results and should be interpreted with caution. In addition, only two samples were analyzed in 1985, and these were highly variable. For example, heterotrophic bacteria counts increased from 12000 to 28500 organisms/100 mL between the two samples, which were collected on the same sampling day. This lack of replicate data prohibits testing of the statistical significance of the apparent increase between years. The total coliform counts in both 1984 and 1985 are considerably reduced from those reported in 1978 (prior to the installation of secondary treatment), when counts of over 1 million/100 mL were found in the effluent (Pugh 1979).

Table 4. Water Pollution Control Plant (WPCP) effluent characteristics for 1984 and 1985.

Parameter	May, 1984				May, 1985			
	n	Median	Mean	S.D.	n	Median	Mean	S.D.
Physical Parameters:								
Colour (app)(HZU)	3	22.0	21.0	1.7	3	17.0	16.7	1.5
Conductivity (25oC) (umho/cm)	3	479.0	479.0	1.5	4	477.0	473.0	36.5
T.D.S. (mg/L)	3	327	321	11	4	313	314	4
T.S.S. (mg/L)	3	3.0	2.7	0.6	4	2.1	3.9	4.1
Total Solids (mg/L)	3	330	323	12	4	318	318	4
Turbidity (NTU)	3	1.30	1.27	0.06	4	0.95	1.81	1.85
Inorganics:								
Chloride (mg/L)	3	23.0	24.0	3.6	4	33.6	33.8	5.1
Cyanide (mg/L)	-	-	-	-	4	<0.001	<0.002	0.002
pH	3	7.3	7.3	0.1	4	7.2	7.2	0.1
Sodium	3	35.00	35.00	0.00	4	33.64	34.01	5.15
Sulphate (mg/L)	2	26.9	26.9	0.3	4	27.8	28.2	1.1
Metals: (mg/L unless otherwise noted)								
Aluminum	3	0.041	0.037	0.006	4	0.160	0.280	0.350
Arsenic	3	<0.001	<0.001	0	4	<0.001	<0.001	0
Barium	3	0.006	0.006	0.001	4	0.008	0.029	0.044
Cadmium	3	0.0003	0.0003	0.0001	4	0.0003	0.0003	0
Cobalt	3	<0.001	<0.001	0	-	-	-	-
Chromium	3	0.002	0.002	0.006	-	-	-	-
Copper	3	0.014	0.012	0.004	-	-	-	-
Iron	3	0.018	0.022	0.011	4	0.365	0.365	0.563
Lead	3	<0.003	<0.003	0	4	0.012	0.012	0.008
Mercury (ug/L)	3	<0.05	<0.05	0	4	<0.05	<0.05	0
Nickel	3	0.001	0.001	0.006	-	-	-	-
Selenium	3	<0.001	<0.001	0	-	-	-	-
Silver	3	<0.005	<0.005	0	-	-	-	-
Zinc	3	0.031	0.033	0.004	4	0.040	0.046	0.051
Nutrients:								
Ammonia (mg/L)	3	0.39	0.48	0.41	4	0.60	0.52	0.35
Nitrate (mg/L)	3	16.0	14.0	3.5	4	6.8	7.4	1.7
TKN (mg/L)	3	1.7	1.8	0.6	3	1.2	1.3	0.6
Phosphorous (total)(mg/L)	3	3.50	3.40	0.30	2	1.50	1.50	0.04
Microbiological: (cnt/100mL)								
<i>Escherichia coli</i>	1	<4	<4	-	-	-	-	-
Fecal coliforms	1	<4	<4	-	-	-	-	-
Fecal streptococci	1	<4	<4	-	-	-	-	-
Heterotrophs	1	4950	4950	-	2	20250	20250	11667
<i>Pseudomonas aeruginosa</i>	1	<4	<4	-	-	-	-	-
Total coliforms	1	<4	<4	-	1	>1500	>1500	-
Total coliforms (background)	1	220	220	-	2	5500	5500	2121

continued ...

Table 4. Water Pollution Control Plant (WPCP) effluent characteristics for 1984 and 1985 (continued).

Parameter	May, 1984				May, 1985			
	n	Median	Mean	S.D.	n	Median	Mean	S.D.
Organics:								
BOD5 (mg/L)	3	1.50	1.43	0.21	4	1.75	2.35	2.08
COD (mg/L)	3	13.0	18.3	12.9	4	15.6	18.2	7.2
DOC (mg/L)	2	4.1	4.1	0.4	4	4.3	4.3	0.7
Phenolics (total) (ug/L)	3	<0.2	<0.2	0	4	0.8	1.1	0.7
Tannins (mg/L)	3	1	1	0	4	1	1	0
Resin Acids: (ug/L)								
Abietic Acid	3	<10	<10	0	4	<10	<10	0
Dehydroabietic Acid	3	<10	<10	0	4	<10	<10	0
Isopimaric Acid	3	<10	<10	0	4	<10	<10	0
Levopimaric Acid	3	<10	<10	0	4	<10	<10	0
Neobietic Acid	3	<10	<10	0	4	<10	<10	0
Pimaric Acid	3	<10	<10	0	4	<10	<10	0
Palustic Acid	3	<10	<10	0	4	<10	<10	0
Sandaracopimaric Acid	3	<10	<10	0	4	<10	<10	0
Fatty Acids: (ug/L)								
Arachidic Acid	3	<10	<10	0	4	<10	<10	0
Capric Acid	3	<10	<10	0	4	<10	<10	0
Lauric Acid	3	<10	<10	0	4	<10	<10	0
Linoleic Acid	3	<10	<10	0	4	<10	<10	0
Myristic Acid	3	<10	<10	0	4	<10	<12	5
Oleic Acid	3	<10	<10	0	4	<10	<85	150
Palmitic Acid	3	<10	<10	0	4	<10	<48	75
Stearic Acid	3	<10	<10	0	4	<10	<24	28
Aromatic Acids: (ug/L)								
Benzoic Acid	3	<10	<10	0	-	-	-	-
Salicylic Acid	3	<10	<10	0	-	-	-	-
Phthalic Acid	3	<10	<10	0	-	-	-	-
Volatile Organohalides: (ng/L unless otherwise noted)								
Hexachlorobutadiene	-	-	-	-	4	<1	<1	0
Chloroform (ug/L)	2	2.5	2.5	0.7	4	5.0	6.3	4.7
Carbon tetrachloide (ug/L)	2	1	1	0	-	-	-	-
Trichloroethylene (ug/L)	2	<1	<1	0	-	-	-	-
Dichlorobromoethane (ug/L)	2	<1	<1	0	4	1.0	1.5	1.0
Chlorodibromoethane (ug/L)	-	-	-	-	4	ND	ND	0
Tetrachloroethylene (ug/L)	2	<1	<1	0	-	-	-	-
Hexachlorobenzene	3	<1	<1	0	4	<1	<1	0
Hexachloroethane	-	-	-	-	4	<1	<1	0
Octachlorostyrene	-	-	-	-	4	<1	<1	0
Pentachlorobenzene	-	-	-	-	4	<1	<1	0
Trihalomethanes (total) (ug/L)	-	-	-	-	4	6.0	7.8	5.7
2,3,6-trichlorotoluene	-	-	-	-	4	<5	<5	0
2,4,5-trichlorotoluene	-	-	-	-	4	<5	<5	0
2,6,A-trichlorotoluene	-	-	-	-	4	<5	<5	0
1,2,3-trichlorobenzene	-	-	-	-	4	<5	<5	0

continued . . .

Table 4. Water Pollution Control Plant (WPCP) effluent characteristics for 1984 and 1985 (continued).

Parameter	May, 1984				May, 1985			
	n	Median	Mean	S.D.	n	Median	Mean	S.D.
Volatile Organohalides (cont.): (ng/L unless otherwise noted)								
1,2,3,4-tetrachlorobenzene	-	-	-	-	4	<1	<1	0
1,2,3,5-tetrachlorobenzene	-	-	-	-	4	<1	<1	0
1,2,4-trichlorobenzene	-	-	-	-	4	<5	<5	0
1,2,4,5-tetrachlorobenzene	-	-	-	-	4	<1	<1	0
1,3,5-trichlorobenzene	-	-	-	-	4	<5	<5	0
Chlorinated Phenolics: (1984: ug/L, 1985: ng/L, unless otherwise noted)								
2-chlorophenol	2	ND	ND	0	3	ND	ND	0
4-chlorophenol	2	ND	ND	0	3	ND	ND	0
2,4-dichlorophenol	2	ND	ND	0	3	ND	ND	0
2,3,4-trichlorophenol(*) (ng/L)	3	<100	<100	0	4	<100	<100	0
2,4,5-trichlorophenol	2	ND	ND	0	3	ND	ND	0
2,4,5-trichlorophenol(*) (ng/L)	3	<50	<50	0	4	<50	<50	0
2,4,6-trichlorophenol	2	ND	ND	0	3	ND	ND	0
2,4,6-trichlorophenol(*) (ng/L)	3	<50	<53	6	4	<50	<50	0
2,3,4,5-tetrachlorophenol	2	ND	ND	0	3	ND	ND	0
2,3,4,5-tetrachlorophenol(*) (ng/L)	3	<50	<50	0	4	<50	<50	0
2,3,5,6-tetrachlorophenol(*) (ng/L)	3	<50	<50	0	4	<50	<50	0
2,4,5,6-tetrachlorophenol	2	ND	ND	0	3	ND	ND	0
Pentachlorophenol	2	ND	ND	0	3	ND	ND	0
Pentachlorophenol (*) (ng/L)	-	-	-	-	4	<50	<50	0
Chloro-p-cresol	2	ND	ND	0	3	ND	ND	0
Speciated Phenolics: (1984: ug/L, 1985: ng/L, unless otherwise noted)								
Phenol	2	ND	ND	0	3	23	<35	43
Vanilline	1	ND	ND	-	3	22	<37	47
Homovanillic Acid	2	ND	ND	0	3	ND	<10	17
Guaiacol	2	ND	ND	0	3	11	<8	7
Syringaldehyde	2	ND	ND	0	3	ND	ND	0
Acetovanillone	2	ND	ND	0	3	14	<10	9
Acetosyringone	2	ND	ND	0	3	ND	ND	0
p-cresol	2	ND	ND	0	3	ND	ND	0
2,4-xyleneol	2	ND	ND	0	3	ND	ND	0
Pesticides: (ng/L)								
Aldrin	3	<1	<1	0	4	<1	<1	0
alpha-BHC	3	<1	<1	0	4	1.5	<2.3	1.9
beta-BHC	3	<1	<1	0	4	<1	<1	0
gamma-BHC	3	<1	<3	3.5	4	35	<33	26
alpha-chlordane	3	<2	<2	0	4	<2	<2	0
gamma-chlordane	3	<2	<2	0	4	<2	<2	0
Dieldrin	3	<2	<2	0	4	<2	<2	0
Methoxychlor	3	<5	<5	0	4	<5	<5	0
Endrin	3	<4	<4	0	4	<4	<4	0
Endosulfan Sulphate	3	<4	<4	0	4	<4	<4	0
Endosulfan I	3	<2	<2	0	4	<2	<2	0
Endosulfan II	3	<4	<4	0	4	<4	<4	0
Heptachlorepoide	3	<1	<1	0	4	<1	<1	0

continued . . .

Table 4. Water Pollution Control Plant (WPCP) effluent characteristics for 1984 and 1985 (concluded).

Parameter	May, 1984				May, 1985			
	n	Median	Mean	S.D.	n	Median	Mean	S.D.
Pesticides (cont.): (ng/L)								
Heptachlor	3	<1	<1	0	4	<1	<1	0
Mirex	3	<5	<5	0	4	<5	<5	0
Oxychlordan	3	<2	<2	0	4	<2	<2	0
o,p'-DDT	3	<5	<5	0	2	<5	<5	0
PCB (total)	3	<2	<20	0	4	<2	<20	0
p,p'-DDD	3	<5	<5	0	4	<5	<5	0
p,p'-DDE	3	<1	<1	0	4	<1	<1	0
p,p'-DDT	3	<5	<5	0	4	<5	<5	0
Dicamba	-	-	-	-	4	<1	<100	0
Picloram	-	-	-	-	4	<1	<100	0
Silvex	-	-	-	-	4	<5	<50	0
2,4-D	-	-	-	-	4	<1	<100	0
2,4-DB	-	-	-	-	4	<2	<200	0
2,4-DP	-	-	-	-	4	<1	<100	0
2,4,5-T	-	-	-	-	4	<5	<50	0

Explanatory Notes:

n	Number of samples analyzed
S.D.	Standard Deviation about the mean
<	One or more individual values were less than the minimum reportable amount.
ND	Not detected; MRA unknown.
-	Analyses not done
(*)	Analysis done by the Drinking Water Lab, as opposed to the Trace Organics Lab.

Table 5. t-test comparisons of 1984 and 1985 Marathon Water Pollution Control Plant (WPCP) effluent.

Parameter	d.f.	t-statistic	$t_{\alpha/2,0.05}$	Significant
<u>Physical Parameters:</u>				
Colour (apparent)	4	3.250	2.776	Yes (D)
Conductivity (25°C)	5	0.305	2.571	No
Total Dissolved Solids	5	1.133	2.571	No
Total Suspended Solids	5	0.513	2.571	No
Total Solids	5	0.891	2.571	No
Turbidity	5	0.496	2.571	No
<u>Inorganics:</u>				
Chloride (reactive)	5	2.799	2.571	Yes (I)
pH	5	1.324	2.571	No
Sodium	5	0.447	2.571	No
Sulphate	4	1.514	2.776	No
<u>Metals:</u>				
Aluminum	5	1.174	2.571	No
Barium	5	0.870	2.571	No
Iron	5	1.030	2.571	No
Lead	5	1.860	2.571	No
Zinc	5	0.515	2.571	No
<u>Nutrients:</u>				
Ammonia	5	0.153	2.571	No
Nitrate	5	3.347	2.571	Yes (D)
TKN	4	1.094	2.776	No
Phosphorous	3	7.664	3.182	Yes (D)
<u>Organics:</u>				
BOD ₅	5	0.742	2.571	No
COD	5	0.014	2.571	No
DOC	4	0.456	2.776	No
Phenolics (total)	5	2.174	2.571	No
<u>Volatile Organohalides:</u>				
Chloroform	4	1.056	2.776	No

- (I) Increase from 1984 to 1985.
 (D) Decrease from 1984 to 1985.

The biochemical and chemical oxygen demand (BOD₅ and COD) of the effluent are low, and relatively constant between years. Total phenolics and chloroform concentrations increased slightly, but not significantly, between 1984 and 1985. Trihalomethanes were measured only in 1985, and were present in low concentrations. These compounds are frequently produced by the chlorination of wastes containing organic compounds. The apparent increase in speciated phenolics from 1984 to 1985 is probably the result of the lower detection limits and concentration units used in 1984.

Low concentrations of the pesticides α -BHC (the most soluble isomer of hexachlorocyclohexane) and γ -BHC (also known as lindane) were detected. Four fatty acids (myristic, oleic, palmitic and stearic acid) were detected in one sample only in 1985. These compounds are commonly associated with pulp and paper mill effluents. All other organic parameters were not detected in the WPCP effluent.

Municipal wastewater treatment facilities discharging to surface waters must meet general OMOE effluent requirements for 5-day Biochemical Oxygen Demand (BOD₅) and Total Suspended Solids (TSS) as outlined in OMOE Policy 08-01 "Levels of Treatment of Municipal and Private Sewage Treatment Works Discharging to Surface Waters" (OMOE 1987). For plants with secondary treatment, these requirements are 25 mg/L for both BOD₅ and TSS, based on annual average values. In addition, WPCPs discharging to Lake Superior must meet the Total Phosphorous (TP) requirement of 1.0 mg/L for the Upper Great Lakes, as specified in the Great Lakes Water Quality Agreement (GLWQA) of 1978 (1988). This criteria is based on a monthly average basis.

The Marathon WPCP was well below the general requirement for BOD₅ and TSS in both years. Levels were less than 3.0 mg/L of BOD₅ and less than 4.0 mg/L of TSS in both 1984 and 1985. TP concentrations slightly exceeded the GLWQA value of 1.0 mg/L in both years, with mean values of 3.5 mg/L and 1.5 mg/L in 1984 and 1985 respectively. The 1984 values are slightly lower than the annual average values of 3.4 mg/L of BOD₅ and 5.8 mg/L of TSS, and slightly higher than the TP annual average of 2.67 mg/L (OMOE 1985b). The 1985 values agree well with the 1985 annual averages of 2.1 mg/L of BOD₅ and 3.6 mg/L of TSS, and are slightly lower than the TP annual average of 3.03 mg/L (OMOE 1986).

3.1.2 Pulp and Paper Mill Effluent

Tables 6 and 7 summarize the James River - Marathon Limited pulp and paper mill effluent and intake data, respectively, collected in 1984 and 1985. Tables 8 and 9 summarize the t-test comparisons made between years for the effluent and intake, respectively, for all parameters for which there were sufficient number of observations. Tables 10 and 11 summarize effluent and pulp production information collected by James River - Marathon Limited during the 1984 and 1985 surveys, respectively.

Kraft pulp mills in Ontario have historically been regulated on the basis of "conventional pollutants" such as TSS and BOD₅. Acute lethality and nutrient concentrations were also used in developing control orders for individual mills. Prior to 1960, suspended solids were probably the most significant pollutant discharged from kraft mills because excessive softwood fibers blanketed the bottom of the receiving water body, destroying fish habitat. In addition, decomposition of the fibers resulted in anoxic conditions and the formation of toxic gases, such as sulfides. However, these problems have largely been alleviated in recent years (Bonser et al. 1988), particularly for the James River - Marathon mill. The control order issued on April 25, 1984 for this mill set the regulatory limit for TSS at 9.0 tonnes/day, based on a 30 day average. The mill was meeting this limit in May, 1984, with a monthly average value of 8.39 tonnes/day (Table 10). By May, 1985 suspended solids were reduced to a monthly average of 4.42 tonnes/day (Table 11). On December 31, 1985, the TSS control order limit was reduced to 6.0 tonnes/day.

The monthly pulp production averages for May were lower than the yearly averages in both years. Several operating problems encountered during May of both years reduced monthly production below the average operation levels. Therefore the loadings listed in Tables 10 and 11 may underestimate typical conditions.

In the effluent characterization conducted in this study, there was no significant change in the concentration of TSS in the mill effluent from 1984 to 1985. However, the concentrations of total dissolved solids (TDS) and total solids (TS) decreased significantly during this time. Turbidity of the effluent increased significantly from a mean value of 5.6 NTU in 1984 to a mean value of 19.2 NTU in 1985 (Table 8).

Table 6. James River - Marathon Limited Pulp and Paper Mill effluent characteristics for 1984 and 1985.

Parameter	May, 1984				May, 1985			
	n	Median	Mean	S.D.	n	Median	Mean	S.D.
Physical Parameters:								
Colour (true)(HZU)	5	1665	1890	546	4	1524	1534	180
Conductivity (25°C) (umho/cm)	5	2410	2480	280	5	2250	2150	258
T.D.S. (mg/L)	5	1700	1727	166	6	1420	1395	134
T.S.S. (mg/L)	5	30.0	33.0	11.0	6	26.2	27.7	10.2
Total Solids (mg/L)	5	1730	1760	174	6	1422	1409	141
Turbidity (NTU)	5	6.0	5.6	2.5	4	17.0	19.2	11.5
Inorganics:								
Chloride (mg/L)	5	535	530	67	5	472	466	57
Cyanide (mg/L)	-	-	-	-	2	0.009	0.009	0.004
pH	5	3.4	4.1	1.7	4	3.2	3.2	0.2
Sodium	5	386.00	380.00	35.78	5	305.88	321.30	64.18
Sulphate (mg/L)	5	54.9	99.8	61.7	5	153.1	152.8	127.4
Sulphur Dioxide (mg/L)	-	-	-	-	3	0	0	0
Metals: (mg/L unless otherwise noted)								
Aluminum	5	0.520	0.580	0.252	3	0.770	0.633	0.290
Arsenic	5	<0.001	<0.001	0.0005	4	<0.001	<0.001	0
Barium	5	0.067	0.062	0.023	3	0.087	0.081	0.016
Cadmium	5	0.0010	0.0016	0.0013	3	0.0003	0.0003	0.0000
Cobalt	5	0.003	0.005	0.004	-	-	-	-
Chromium	5	0.006	0.006	0.004	-	-	-	-
Copper	5	0.010	0.006	0.004	-	-	-	-
Iron	5	0.490	0.698	0.353	3	1.180	1.023	0.571
Lead	5	<0.003	<0.003	0	3	0.014	0.015	0.003
Mercury (ug/L)	5	0.12	1.59	2.37	5	0.09	0.08	0.03
Nickel	5	0.010	0.007	0.006	-	-	-	-
Selenium	4	<0.001	<0.001	0	-	-	-	-
Silver	5	<0.005	<0.005	0	-	-	-	-
Zinc	5	0.086	0.093	0.039	3	0.052	0.051	0.024
Nutrients:								
Ammonia (mg/L)	5	1.80	<1.48	0.83	5	1.47	1.59	0.46
Nitrate (mg/L)	5	0.39	0.40	0.07	5	0.18	0.31	0.27
TKN (mg/L)	5	2.5	2.5	0.3	6	2.5	2.7	1.5
Phosphorous (total)(mg/L)	5	0.45	0.46	0.34	5	0.38	0.34	0.12
Microbiological: (cnt/100mL)								
<i>Escherichia coli</i>	1	<10	<10	-	-	-	-	-
Fecal coliforms	1	<10	<10	-	-	-	-	-
Fecal streptococci	1	<10	<10	-	-	-	-	-
Heterotrophs	1	10	10	-	2	7.5	7.5	3.5
<i>Pseudomonas aeruginosa</i>	1	<10	<10	-	-	-	-	-
Total coliforms	1	<10	<10	-	2	<10	<10	0
Total coliforms (background)	1	<10	<10	-	2	<10	<10	0
Organics:								
BOD5 (mg/L)	5	205	212	20	4	198	195	7

continued ...

Table 6. James River - Marathon Limited Pulp and Paper Mill effluent characteristics for 1984 and 1985 (continued).

Parameter	May, 1984				May, 1985			
	n	Median	Mean	S.D.	n	Median	Mean	S.D.
Organics (cont.):								
COD (mg/L)	5	860	909	119	6	1425	1418	211
DOC (mg/L)	5	245	250	19	6	251	446	493
Phenolics (total) (ug/L)	5	2240	2086	307	6	2200	2247	513
Tannins (mg/L)	5	100	97	34	4	125	125	29
Resin Acids: (ug/L)								
Abietic Acid	4	1010	850	395	4	355	405	374
Dehydroabietic Acid	4	1380	1360	539	4	435	421	264
Isopimaric Acid	4	185	198	91	4	35	35	18
Levopimaric Acid	5	<10	<14	6	4	<10	<10	0
Neobietic Acid	5	<10	<18	11	4	<10	<10	0
Pimaric Acid	4	165	148	53	4	60	55	37
Palustric Acid	5	<10	<14	9	4	<10	<10	0
Sandaracopimaric Acid	5	120	114	68	4	102	96	38
Fatty Acids: (ug/L)								
Arachidic Acid	5	<10	<10	0	4	<13	<13	3
Capric Acid	5	<10	<10	0	4	<10	<10	0
Lauric Acid	5	<10	<10	0	4	<10	<10	0
Linoleic Acid	4	1095	1193	331	4	355	353	220
Myristic Acid	5	<10	<10	0	4	<10	<10	0
Oleic Acid	4	345	313	90	4	150	<163	177
Palmitic Acid	4	240	220	54	4	70	61	25
Stearic Acid	4	345	313	90	4	25	<23	10
Aromatic Acids: (ug/L)								
Benzoic Acid	5	<10	<12	5	-	-	-	-
Salicylic Acid	5	<10	<14	6	-	-	-	-
Phthalic Acid	5	<10	<10	0	-	-	-	-
Volatile Organohalides: (ng/L unless otherwise noted)								
Chloroform (ug/L)	2	2350	2350	1287	4	3509	3491	375
Carbon tetrachloride (ug/L)	2	23	23	14	-	-	-	-
Trichloroethylene (ug/L)	2	<1	<1	0	-	-	-	-
Dichlorobromomethane (ug/L)	2	<1	<1	0	4	ND	ND	0
Chlorodibromoethane (ug/L)	-	-	-	-	4	ND	ND	0
Tetrachloroethylene (ug/L)	2	2.0	2.0	1.4	-	-	-	-
Hexachlorobenzene	5	<1	<1	0	6	<1	<1	0
Chlorinated Phenolics: (1984: ug/L, 1985: ng/L, unless otherwise noted)								
2-chlorophenol	5	ND	ND	0	4	ND	ND	0
4-chlorophenol	5	ND	ND	0	4	ND	ND	0
2,4-dichlorophenol	5	ND	ND	0	4	ND	ND	0
2,3,4-trichlorophenol(*) (ng/L)	5	<100	<100	0	6	<100	<100	0
2,4,5-trichlorophenol	5	ND	ND	0	4	ND	ND	0
2,4,5-trichlorophenol(*) (ng/L)	3	<50	<50	0	6	<50	<50	0
2,4,6-trichlorophenol	5	ND	ND	0	4	ND	ND	0
2,4,6-trichlorophenol(*) (ng/L)	3	6700	7020	2244	6	<50	<50	0

continued ...

Table 6. James River - Marathon Limited Pulp and Paper Mill effluent characteristics for 1984 and 1985 (concluded).

Parameter	May, 1984				May, 1985			
	n	Median	Mean	S.D.	n	Median	Mean	S.D.
Chlorinated Phenolics (cont.): (1984: ug/L, 1985: ng/L, unless otherwise noted)								
2,3,4,5-tetrachlorophenol	5	ND	ND	0	4	ND	ND	0
2,3,4,5-tetrachlorophenol(*) (ng/L)	5	<50	<50	0	6	<50	<50	0
2,3,5,6-tetrachlorophenol(*) (ng/L)	5	<50	<50	0	6	<50	<50	0
2,4,5,6-tetrachlorophenol	5	ND	ND	0	4	ND	ND	0
Pentachlorophenol	5	ND	ND	0	4	ND	ND	0
Pentachlorophenol(*) (ng/L)	-	-	-	-	6	380	<405	266
Chloro-p-cresol	5	ND	ND	0	4	ND	ND	0
Speciated Phenolics: (1984: ug/L, 1985: ng/L, unless otherwise noted)								
Phenol	5	48	46	5	4	20600	20469	22554
Vanilline	5	308	366	111	4	101250	124375	88327
Homovanillic Acid	5	372	386	134	4	445	<90222	189000
Guaiacol	5	3090	3280	391	4	1790000	3370000	4060000
Syringaldehyde	5	ND	ND	0	4	ND	ND	0
Acetovanillone	5	208	234	142	4	115000	271000	373000
Acetosyringone	5	ND	ND	0	4	ND	ND	0
p-cresol	5	ND	ND	0	4	ND	ND	0
2,4-xyleneol	5	ND	ND	0	4	ND	ND	0
Pesticides: (ng/L)								
Aldrin	5	<1	<1	0	6	<1	<1	0
alpha-BHC	5	<1	<1	0	6	<1	<1	0
beta-BHC	5	<1	<1	0	6	<1	<1	0
gamma-BHC	5	<1	<1	0	6	<1	<1	0
alpha-chlordane	5	<2	<2	0	6	<2	<2	0
gamma-chlordane	5	<2	<2	0	6	<2	<2	0
Dieldrin	1	86	86	-	2	<2	<2	0
Methoxychlor	2	<5	<5	0	2	<5	<5	0
Endrin	1	<4	<4	-	2	<4	<4	0
Endosulfan Sulphate	1	<4	<4	-	2	<4	<4	0
Endosulfan I	1	170	170	-	2	1	14	11
Endosulfan II	1	<4	<4	-	2	<4	<4	0
Heptachlorepoxyde	1	<1	<1	-	2	<1	<1	0
Heptachlor	5	<1	<1	0	6	<1	<1	0
Mirex	5	<5	<5	0	6	<5	<5	0
Oxychlordane	1	<2	<2	-	2	<2	<2	0
o,p'-DDT	5	<5	<5	0	4	<5	<5	0
PCB (total)	5	<2	<216	438	6	<2	<127	256
p,p'-DDD	5	<5	<5	0	6	<5	<5	0
p,p'-DDE	5	<1	<1	0	6	<1	<1	0
p,p'-DDT	5	<5	<5	0	6	<5	<5	0

Explanatory Notes:

n	Number of samples analyzed
S.D.	Standard Deviation about the mean
<	One or more individual values were less than the minimum reportable amount.
ND	Not detected; MRA unknown.
-	Analyses not done
(*)	Analysis done by the Drinking Water Lab, as opposed to the Trace Organics Lab.

Table 7. James River - Marathon Limited Pulp and Paper Mill intake water characteristics for 1984 and 1985.

Parameter	May, 1984				May, 1985			
	n	Median	Mean	S.D.	n	Median	Mean	S.D.
Physical Parameters:								
Colour (app)(HZU)	3	6.0	6.3	1.5	4	4.5	4.8	1.0
Conductivity (25oC) (umho/cm)	3	106.0	107.7	10.6	4	93.5	93.3	3.3
T.D.S. (mg/L)	3	69.0	67.0	4.0	4	74.8	78.3	13.6
T.S.S. (mg/L)	3	1.0	1.3	0.6	4	0.6	0.7	0.2
Total Solids (mg/L)	3	70.0	68.0	3.0	4	75.6	79.0	13.6
Turbidity (NTU)	3	0.45	0.60	0.26	4	0.48	0.48	0.09
Inorganics:								
Chloride (mg/L)	3	2.50	2.83	1.53	4	1.91	1.89	0.12
Cyanide (mg/L)	-	-	-	-	4	<0.001	<0.001	0.000
pH	3	7.9	7.8	0.2	4	7.6	7.4	0.3
Sodium	3	3.63	3.00	2.41	4	3.25	1.73	3.10
Sulphate (mg/L)	3	3.99	3.86	1.03	3	3.55	3.30	0.55
Metals: (mg/L, unless otherwise noted)								
Aluminum	3	0.020	0.017	0.006	3	0.019	0.013	0.006
Arsenic	3	<0.001	<0.001	0.000	4	<0.001	<0.001	0.000
Barium	3	0.008	0.008	0.000	3	0.009	0.009	0.001
Cadmium	3	0.0002	0.0002	0.0001	3	0.0003	0.0003	0.0000
Cobalt	3	<0.001	<0.001	0.000	-	-	-	-
Chromium	3	<0.001	<0.001	0.000	-	-	-	-
Copper	3	0.001	0.001	0.006	-	-	-	-
Iron	3	0.057	0.044	0.035	3	0.034	0.037	0.008
Lead	3	<0.003	<0.003	0.000	3	<0.003	<0.003	0.000
Mercury (ug/L)	3	<0.05	<0.05	0.00	3	<0.05	<0.05	0.00
Nickel	3	<0.001	<0.001	0.000	-	-	-	-
Selenium	3	<0.001	<0.001	0.000	-	-	-	-
Silver	3	<0.005	<0.005	0.000	-	-	-	-
Zinc	3	0.002	0.002	0.001	3	0.002	0.002	0.001
Nutrients:								
Ammonia (mg/L)	3	<0.010	<0.013	0.006	4	0.006	0.006	0.001
Nitrate (mg/L)	3	0.31	0.31	0.00	4	0.34	0.34	0.02
TKN (mg/L)	3	0.130	0.140	0.020	4	0.085	0.088	0.009
Phosphorous (total)(mg/L)	3	0.006	0.008	0.003	3	0.002	0.002	0.006
Microbiological: (cnt/100mL)								
<i>Escherichia coli</i>	1	<4	<4	1	-	-	-	-
Fecal coliforms	1	<4	<4	1	-	-	-	-
Fecal streptococci	1	<4	<4	1	-	-	-	-
Heterotrophs	1	1700	1700	1	2	6100	6100	778
<i>Pseudomonas aeruginosa</i>	1	<2	<2	1	-	-	-	-
Total coliforms	1	<4	<4	1	2	24	24	6
Total coliforms (background)	1	68	68	1	2	318	318	229

continued . . .

Table 7. James River - Marathon Limited Pulp and Paper Mill intake water characteristics for 1984 and 1985 (continued).

Parameter	May, 1984				May, 1985			
	n	Median	Mean	S.D.	n	Median	Mean	S.D.
Organics:								
BOD5 (mg/L)	3	0.60	0.57	0.25	4	0.35	0.40	0.24
COD (mg/L)	-	-	-	-	4	3.40	3.88	1.90
DOC (mg/L)	3	1.70	1.73	0.15	4	1.50	1.53	0.05
Phenolics (total) (ug/L)	3	0.20	0.47	0.46	4	0.70	<0.90	0.77
Tannins (mg/L)	3	0.00	0.33	0.58	4	0.00	0.00	0.00
Resin Acids: (ug/L)								
Abietic Acid	3	<10	<10	0	4	<10	<10	0
Dehydroabietic Acid	3	<10	<10	0	4	<10	<10	0
Isopimaric Acid	3	<10	<10	0	4	<10	<10	0
Levopimaric Acid	3	<10	<10	0	4	<10	<10	0
Neoabietic Acid	3	<10	<10	0	4	<10	<10	0
Pimaric Acid	3	<10	<10	0	4	<10	<10	0
Palustric Acid	3	<10	<10	0	4	<10	<10	0
Sandaracopimaric Acid	3	<10	<10	0	4	<10	<10	0
Fatty Acids: (ug/L)								
Arachidic Acid	3	<10	<10	0	4	<10	<10	0
Capric Acid	3	<10	<10	0	4	<10	<10	0
Lauric Acid	3	<10	<10	0	4	<10	<10	0
Linoleic Acid	3	<10	<10	0	4	<10	<10	0
Myristic Acid	3	<10	<10	0	4	<10	<10	0
Oleic Acid	3	<10	<10	0	4	<10	<10	0
Palmitic Acid	3	<10	<10	0	4	<10	<10	0
Stearic Acid	3	<10	<10	0	4	<10	<10	0
Aromatic Acids: (ug/L)								
Benzoic Acid	3	<10	<10	0	-	-	-	-
Salicylic Acid	3	<10	<10	0	-	-	-	-
Phthalic Acid	3	<10	<10	0	-	-	-	-
Volatile Organohalides: (ng/L unless otherwise noted)								
Hexachlorobutadiene	-	-	-	-	4	<1	<1	0
Chloroform (ug/L)	2	4.5	4.5	4.9	4	ND	ND	0
Carbon tetrachloride (ug/L)	2	1	1	0	-	-	-	-
Trichloroethylene (ug/L)	2	<1	<1	0	-	-	-	-
Dichlorobromomethane (ug/L)	2	<1	<1	0	4	ND	ND	0
Chlorodibromoethane (ug/L)	-	-	-	-	4	ND	ND	0
Tetrachloroethylene (ug/L)	2	<1	<1	0	-	-	-	-
Hexachlorobenzene	3	<1	<1	0	4	<1	<1	0
Hexachloroethane	-	-	-	-	4	<1	<1	0
Octachlorostyrene	-	-	-	-	4	<1	<1	0
Pentachlorobenzene	-	-	-	-	4	<1	<1	0
Trihalomethanes (total) (ug/L)	-	-	-	-	4	ND	ND	0
2,3,6-trichlorotoluene	-	-	-	-	4	<5	<5	0

continued . . .

Table 7. James River - Marathon Limited Pulp and Paper Mill intake water characteristics for 1984 and 1985 (continued).

Parameter	May, 1984				May, 1985			
	n	Median	Mean	S.D.	n	Median	Mean	S.D.
Volatile Organohalides (cont.): (ng/L unless otherwise noted)								
2,4,5-trichlorotoluene	-	-	-	-	4	<5	<5	0
2,6,A-trichlorotoluene	-	-	-	-	4	<5	<5	0
1,2,3-trichlorobenzene	-	-	-	-	4	<5	<5	0
1,2,3,4-tetrachlorobenzene	-	-	-	-	4	<1	<1	0
1,2,3,5-tetrachlorochlorobenzene	-	-	-	-	4	<1	<1	0
1,2,4-trichlorobenzene	-	-	-	-	-	-	-	-
1,2,4,5-tetrachlorobenzene	-	-	-	-	4	<1	<1	0
1,3,5-trichlorobenzene	-	-	-	-	4	<5	<5	0
Chlorinated Phenolics: (1984: ug/L, 1985: ng/L, unless otherwise noted)								
2-chlorophenol	3	ND	ND	0	4	ND	ND	0
4-chlorophenol	3	ND	ND	0	4	ND	ND	0
2,4-dichlorophenol	3	ND	ND	0	4	ND	ND	0
2,3,4-trichlorophenol(*) (ng/L)	3	<100	<100	0	4	<100	<100	0
2,4,5-trichlorophenol	3	ND	ND	0	4	ND	ND	0
2,4,5-trichlorophenol(*) (ng/L)	3	<50	<50	0	4	<50	<50	0
2,4,6-trichlorophenol	3	ND	ND	0	4	ND	ND	0
2,4,6-trichlorophenol(*) (ng/L)	3	<50	<50	0	4	<50	<50	0
2,3,4,5-tetrachlorophenol	3	ND	ND	0	4	ND	ND	0
2,3,4,5-tetrachlorophenol(*) (ng/L)	3	<50	<50	0	4	<50	<50	0
2,3,5,6-tetrachlorophenol(*) (ng/L)	3	<50	<50	0	4	<50	<50	0
2,4,5,6-tetrachlorophenol	3	ND	ND	0	4	ND	ND	0
Pentachlorophenol	3	ND	ND	0	4	ND	ND	0
Pentachlorophenol(*) (ng/L)	-	-	-	-	4	<50	<50	0
Chloro-p-cresol	3	ND	ND	0	4	ND	ND	0
Speciated Phenolics: (1984: ug/L, 1985: ng/L, unless otherwise noted)								
Phenol	3	ND	ND	0	4	ND	1	2
Vanilline	3	ND	ND	0	4	14.5	15.3	8.3
Homovanillic Acid	3	ND	ND	0	4	ND	ND	0
Guaiacol	3	ND	ND	0	4	7.0	<11.5	15.2
Syringaldehyde	3	ND	ND	0	4	ND	ND	0
Acetovanillone	3	ND	ND	0	4	25.0	<34.5	37.6
Acetosyringone	3	ND	ND	0	4	ND	ND	0
p-cresol	3	ND	ND	0	4	ND	ND	0
2,4-xyleneol	3	ND	ND	0	4	ND	ND	0
Pesticides: (ng/L)								
Aldrin	3	<1	<1	0	4	<1	<1	0
alpha-BHC	3	<1	<1	0	4	5	5	1.8
beta-BHC	2	<1	<1	0	4	<1	<1	0
gamma-BHC	3	<1	<1	0	4	<1	<1	0
alpha-chlordane	3	<2	<2	0	4	<2	<2	0
gamma-chlordane	3	<2	<2	0	4	<2	<2	0
Dieldrin	3	<2	<2	0	4	<2	<2	0
Methoxychlor	3	<5	<5	0	4	<5	<5	0
Endrin	3	<4	<4	0	4	<4	<4	0
Endosulfan Sulphate	3	<4	<4	0	4	<4	<4	0

continued . . .

Table 7. James River - Marathon Limited Pulp and Paper Mill intake water characteristics for 1984 and 1985 (concluded).

Parameter	May, 1984				May, 1985			
	n	Median	Mean	S.D.	n	Median	Mean	S.D.
Pesticides (cont.): (ng/L)								
Endosulfan I	3	<2	<2	0	4	<2	<2	0
Endosulfan II	3	<4	<4	0	4	<4	<4	0
Heptachlorepoide	3	<1	<1	0	4	<1	<1	0
Heptachlor	3	<1	<1	0	4	<1	<1	0
Mirex	3	<5	<5	0	4	<5	<5	0
Oxychlordan	3	<2	<2	0	4	<2	<2	0
o,p'-DDT	3	<5	<5	0	3	<5	<5	0
PCB (total)	3	<2	<20	0	4	<2	<20	0
p,p'-DDD	3	<5	<5	0	4	<5	<5	0
p,p'-DDE	3	<1	<1	0	4	<1	<1	0
p,p'-DDT	3	<5	<5	0	4	<5	<5	0
Dicamba	-	-	-	-	4	<1	<100	0
Picloram	-	-	-	-	4	<1	<100	0
Silvex	-	-	-	-	4	<5	<50	0
2,4-D	-	-	-	-	4	<1	<100	0
2,4-DB	-	-	-	-	4	<2	<200	0
2,4-DP	-	-	-	-	4	<1	<100	0
2,4,5-T	-	-	-	-	4	<5	<50	0

Explanatory Notes:

n	Number of samples analyzed
S.D.	Standard Deviation about the mean
<	One or more individual values were less than the minimum reportable amount.
ND	Not detected; MRA unknown.
-	Analyses not done
(*)	Analysis done by the Drinking Water Lab, as opposed to the Trace Organics Lab.

Table 8. t-test comparisons of 1984 and 1985 James River -Marathon Pulp and Paper Mill effluent.

Parameter	d.f.	t-stat.	$t_{\alpha,0.05}$	Significant
<u>Physical Parameters:</u>				
Colour (true)	7	1.238	2.365	No
Conductivity (25°C)	8	1.939	2.306	No
Total Dissolved Solids	9	3.687	2.262	Yes (D)
Total Suspended Solids	9	0.832	2.262	No
Total Solids	9	3.693	2.262	Yes (D)
Turbidity	7	2.614	2.365	Yes (I)
<u>Inorganics:</u>				
Chloride (reactive)	8	1.636	2.306	No
pH	7	0.972	2.365	No
Sodium	8	2.438	2.306	Yes (D)
Sulphate	8	0.839	2.306	No
<u>Metals:</u>				
Aluminum	6	0.275	2.447	No
Barium	6	1.282	2.447	No
Iron	6	1.017	2.447	No
Lead	6	9.100	2.447	Yes (I)
Mercury	8	1.421	2.306	No
Zinc	6	1.670	2.447	No
<u>Nutrients:</u>				
Ammonia	7	1.107	2.365	No
Nitrate	8	0.684	2.306	No
TKN	9	0.373	2.262	No
Phosphorous	8	1.986	2.306	No
<u>Organics:</u>				
BOD ₅	7	1.612	2.365	No
COD	9	4.770	2.262	Yes (I)
DOC	9	0.879	2.262	No
Phenolics (total)	9	0.612	2.262	No
Tannins	7	1.303	2.365	No
<u>Resin Acids:</u>				
Abietic Acid	6	1.637	2.447	No
Dehydroabietic Acid	6	3.126	2.447	Yes (D)
Pimaric Acid	6	2.857	2.447	Yes (D)
Isopimaric Acid	6	3.499	2.447	Yes (D)
Sandaracopimaric Acid	7	0.465	2.365	No

continued . . .

Table 8. t-test comparisons of 1984 and 1985 James River -Marathon Pulp and Paper Mill effluent (concluded).

Parameter	d.f.	t-stat.	$t_{\alpha/2,0.05}$	Significant
<u>Fatty Acids:</u>				
Palmitic Acid	6	5.336	2.447	Yes (D)
Stearic Acid	6	6.412	2.447	Yes (D)
Oleic Acid	6	1.509	2.447	No
Linoleic Acid	6	4.231	2.447	Yes (D)
<u>Volatile Organohalides:</u>				
Chloroform	4	1.828	2.776	No
<u>Chlorinated Phenolics:</u>				
Phenol	3	0.003	3.182	No
Vanilline	6	3.630	2.447	Yes (D)
Homovanillic Acid	1	1.088	12.706	No
Guaiacol	3	0.044	3.182	No
Acetovanillone	3	0.186	3.182	No
2,4,6-trichlorophenol	9	7.693	2.262	Yes (D)

(I) Increase from 1984 to 1985.

(D) Decrease from 1984 to 1985.

Table 9. t-test comparisons of 1984 and 1985 James River -Marathon Limited intake.

Parameter	d.f.	t-stat.	t _{v,0.05}	Significant
<u>Physical Parameters</u>				
Colour (apparent)	5	1.702	2.571	No
Conductivity (25°C)	5	2.631	2.571	Yes (D)
Total Dissolved Solids	5	1.374	2.571	No
Total Suspended Solids	5	2.240	2.571	No
Total Solids	5	1.306	2.571	No
Turbidity	5	0.992	2.571	No
<u>Inorganics</u>				
Chloride (reactive)	5	1.276	2.571	No
pH	5	1.846	2.571	No
Sodium	5	0.179	2.571	No
Sulphate	4	0.828	2.776	No
<u>Metals:</u>				
Aluminum	4	0.707	2.776	No
Zinc	4	0.500	2.776	No
<u>Nutrients:</u>				
Ammonia	5	2.485	2.571	No
Nitrate	5	2.390	2.571	No
TKN	5	5.196	2.571	Yes (D)
Phosphorous	4	3.124	2.776	Yes (D)
<u>Organics:</u>				
BOD ₅	5	0.881	2.571	No
DOC	5	2.621	2.571	Yes (D)
Phenolics (total)	5	0.850	2.571	No

(I) Increase from 1984 to 1985.

(D) Decrease from 1984 to 1985.

Table 10. Effluent and pulp production data for James River - Marathon Ltd. during 1984 sampling.

Date	Pulp Production (Mt/day)	Effluent Flow (m3/day)	Suspended Solids		BOD5	
			ppm	Mt/day	ppm	Mt/day
May 16, 1984	253.10	65,072	80	5.19	180	11.68
May 19, 1984	531.90	63,779	158	10.06	-	-
May 20, 1984	468.80	68,126	160	10.92	296	20.16
Monthly mean	414.01	62,200	135	8.39	187.84	11.97
Yearly mean	426.84	60,001	83	5.45	-	14.65

Table 11. Effluent and pulp production data for James River - Marathon Ltd. during 1985 sampling.

Date	Pulp Production (Mt/day)	Effluent Flow (m3/day)	Suspended Solids		BOD5	
			ppm	Mt/day	ppm	Mt/day
May 14, 1985	363.70	64,632	42	2.71	185	11.96
May 17, 1985	467.30	71,552	97	6.94	192	13.94
Monthly mean	359.01	65,970	67	4.42	189	12.48
Yearly mean	424.51	69,036	65	4.52	-	13.22

Biochemical oxygen demand is a measure of the tendency of an effluent to consume dissolved oxygen from a receiving water by natural biochemical degradation (Bonser et al. 1988). BOD is standardly measured in North America over a five day period. In 1984 and 1985 the control order limit for BOD₅ at the James River -Marathon mill was 45 kg per air-dried tonne (ADt) of pulp produced. Tables 10 and 11 show daily BOD₅ loadings and pulp production from which production loadings may be calculated. On May 16, 1984, the BOD₅ loading slightly exceeded this limit at 46 kg/ADt. This may have been due to reduced pulp production on this day. Loadings on May 20, 1984 were 43 kg/ADt, and the monthly average was 29 kg/ADt. The yearly average loading was 34 kg/ADT. In 1985, loadings were below the regulatory limit on all occasions, with loadings of 33 kg/ADt and 30 kg/ADt on May 14 and May 17, respectively. Monthly and yearly average loadings were 35 kg/ADt and 31 kg/ADt, respectively.

In the effluent samples collected in this study, BOD₅ concentrations did not change significantly between years. However, chemical oxygen demand (COD) increased significantly from 1984 to 1985 (Tables 6 and 8). COD is a measure of the oxygen equivalent of the organic matter present in an effluent that is susceptible to oxidation by a strong chemical oxidant (Standard Methods 15th ed. 1980).

Sodium compounds, such as sodium sulphide and sodium hydroxide, are used in the pulping and bleaching processes at the pulp mill. High values of sodium are thus commonly found in kraft mill effluents. Sodium concentrations decreased significantly from a mean value of 380 mg/L in 1984 to a mean value of 321 mg/L in 1985.

Of the other inorganic constituents of the effluent samples taken in this study, sulphate concentrations were fairly high, and increased slightly from 1984 to 1985. This increase was not significant at the 5% confidence level, probably because of the variability associated with the 1985 data. Metals concentrations were generally low, and remained constant between years, with the exception of a significant increase in lead. The reason for this is unknown. Aluminum concentrations increased slightly, but not significantly. Although mercury concentrations were reduced from a mean value of 1.59 mg/L in 1984 to 0.08 mg/L in 1985, this increase is not statistically significant because of the variability associated with the 1984 data. These concentrations are higher than the average effluent mercury concentration of .0045 mg/L found in the American Can effluent in 1976 (Tomlinson 1978).

Nutrient concentrations were considerably elevated from the intake water, but remained generally unchanged between years. Total phosphorous concentrations were less than 0.5 mg/L in both years. Microbiological counts were, with the exception of low numbers of heterotrophic bacteria, below detection level. As the fecal coliform method employed in this study also includes *Klebsiella pneumoniae* counts (a bacteria commonly associated with pulp mill effluents), the low numbers indicate that this bacterial contamination is not a problem with this mill.

Chloroform is often found in appreciable amounts in mills such as James River - Marathon Limited that use a hypochlorite bleaching stage. The mean values of chloroform in the effluent were 2350 µg/L in 1984 and 3491 µg/L in 1985. This increase is not statistically significant because of the variability of the 1984 data. It does, however, indicate that chloroform concentrations may be increasing. Although identified as a potential hazardous pollutant, the toxicity and bioaccumulation of chloroform is low in aquatic organisms. It is primarily of concern as human health hazard to workers exposed at the mill because of its volatility and suspected carcinogenicity (Bonser et al. 1988).

The pesticides dieldrin and Endosulfan I were detected at appreciable levels in the 1984 effluent samples. However, these are single sample results and are therefore not conclusive.

Polychlorinated biphenyls (PCB's) appear to have decreased from 1984 to 1985. However, the mean values are based on only one or two values above the detection limit, and may represent anomalous results. The mean values were not significantly different between years. PCB's were detected in one out of four (20%) of the mill effluent samples in 1984 and in two out of six samples (33%) in 1985, and were not detected in the intake water samples. It thus appears that leakage and spills from the equipment used in the mill may still be an active point source of the compounds.

The toxic components associated with pulp mill effluents (resin acids, fatty acids and phenolic compounds) exhibited the most dramatic changes between years. Of the resin acids, dehydroabietic acid, pimaric acid and isopimaric acid decreased significantly from 1984 to 1985. Abietic acid and sandaracopimaric acid showed similar, although non-significant, decreases. During the 1984 sampling period, the mill was processing exclusively softwoods for pulp production. In 1985, the mill changed from a softwood run to a hardwood run during the sampling period. Hardwood runs occurred

approximately once every five weeks in 1985. Softwoods (such as pine) generally contain higher concentrations of resinous material. The apparent decrease in resin acids between years may thus actually reflect differences in the furnish used.

Three of the fatty acids (palmitic acid, stearic acid and linoleic acid) also decreased significantly. Oleic acid also decreased slightly. Of the speciated and chlorinated phenolic compounds, vanillin and 2,4,6-trichlorophenol decreased significantly. The decrease in vanillin concentrations may be partially attributed to the 1985 change in method sensitivity and reporting units noted for the WPCP effluent. Total reactive phenolics in the effluent were high (greater than 2000 $\mu\text{g/L}$), but relatively the same between years.

Tables 4, 6, and 7 show apparently duplicate analyses for the chlorinated phenolic compounds. The samples marked with (*) were analyzed in scans performed by the Drinking Water Laboratory, as opposed to those performed by the Trace Organics Laboratory. The Drinking Water Laboratory is designed to analyze trace amounts of these chemicals, hence detectable levels may be indicated for compounds that could not be detected in the analyses done by the Trace Organics Laboratory. In addition, the Drinking Water Laboratory analyses are reported in ng/L , as opposed to $\mu\text{g/L}$. Pentachlorophenol was detected at approximately 400 ng/L in 1985 by the Drinking Water Laboratory. Pentachlorophenol was not analyzed by this lab in the 1984 effluent samples.

Despite this apparent decrease in the concentration of toxic components during these sampling periods, the mill effluent continues to be highly toxic to fish. In 1986 the 96 hour LC_{50} of the mill effluent for rainbow trout was 12 - 15%. This means that the effluent must be diluted to 12 - 15% of its initial concentration before 50% of the rainbow trout can survive in it for 96 hours. The high toxicity implies that the observed decrease in toxic components is a temporary phenomenon associated with hardwood runs.

The mill intake water was primarily analyzed to eliminate the possibility of source water quality changes contributing to effluent quality changes. A comparison of Tables 8 and 9 shows that the parameters exhibiting significant differences in concentration between years in the mill effluent and intake water are completely exclusive. It thus appears that changes in the mill effluent quality are fully independent of the quality of the intake water. The large number of values below the minimum reportable amount, and the differences in variability between years, prohibited any quantitative or statistical comparison of effluent and source concentrations.

The mill intake water is withdrawn from Jellicoe Cove, and as such is indicative of the water quality in this embayment. The intake water shows possible minor influences from the WPCP and mill effluents. Counts of heterotrophic and total coliforms (background) are somewhat elevated, indicating possible influence from the WPCP effluent. Significant decreases in Total Kjeldahl Nitrogen (TKN) and total phosphorous may be related to similar significant decreases in nutrients in the WPCP effluent. Low concentrations of chloroform (detected in 1984 only) and of the speciated phenolics vanillin, guaiacol, and acetovanillon may be associated with the pulp and paper mill effluent.

3.2 WATER QUALITY

3.2.1 Effluent Plume

The plume tracking efforts were generally unsuccessful because of the variable wind conditions characteristic of Lake Superior. When the drogues were deployed on the morning of May 23, 1985, the prevailing winds were from the north by northeast. At 12:30 the wind direction changed radically to the west. At 13:10 the winds again shifted, coming from the southwest. These erratic winds made it impossible to establish the configuration and extent of the surface plume.

This tracking exercise confirms earlier observations that the spatial configuration of the plume is strongly governed by wind direction (Herzog and Chatterjee 1974). Plume tracking studies conducted by Beak Consultants Limited (1986) in June 1986 further verified the erratic nature of the plume. On June 18 the surface plume extended from the diffuser to the northwest around the peninsula into the mouth of Peninsula Harbour. However, on June 20 the plume was bounded by the shore to the north and was located generally to the east of the diffuser.

Although no plume tracking was conducted during the water sampling surveys on May 14 and 17, 1985, general observations on plume delineation were made. On May 14 at 10:45, the winds were calm and from the northeast, and the surface plume was barely visible. The winds increased slightly in velocity at 14:00. The mill was experiencing mechanical difficulties with the boilers during this day, and was thus not running at full softwood production. On May 17, the winds were calm and from the southwest. The mill was running at full capacity and a visible surface plume was evident. The plume extended east from the diffuser, following the shoreline. As both survey days were relatively calm, the

conditions were representative of a "worse-case scenario" for discharged mill effluents because dilution would be minimized with reduced wind-driven currents.

3.2.2 Depth Profiles

The depth profiles conducted at the stations within the harbour and in open Lake Superior showed relative uniformity of conductivity, water temperature and dissolved oxygen (1984 only) from the surface to the bottom. These results indicate a well-mixed water column.

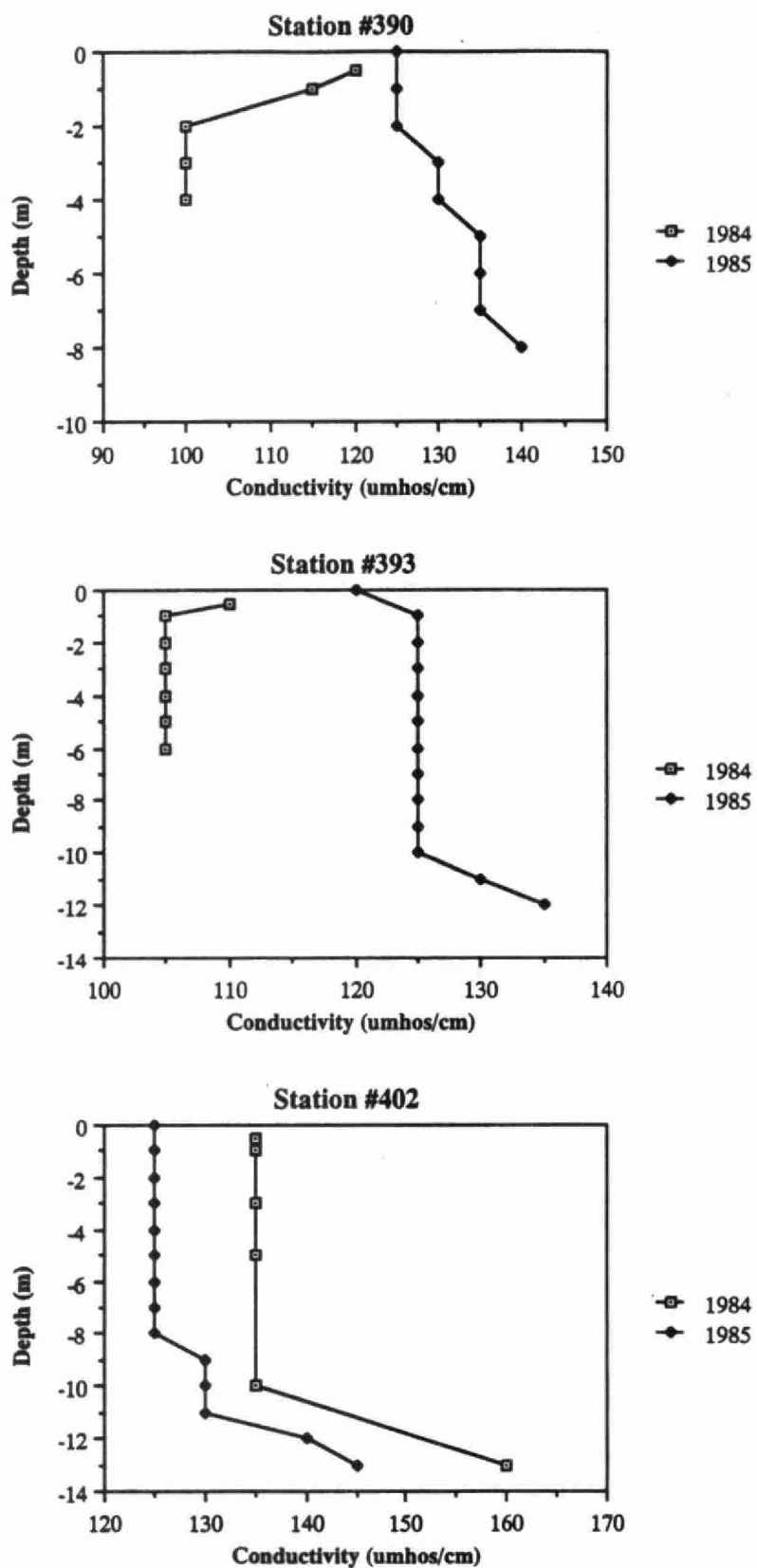
Stations #390, #393 and #402, near the mill and WPCP outfalls, showed minor variations in conductivity and water temperature throughout the water column in both years. The profiles of these stations also changed from 1984 to 1985. Figures 6 and 7 illustrate the depth profiles for conductivity and water temperature, respectively, for these three stations in both years. The lack of dissolved oxygen data in 1985 prohibits comparison of this parameter between years.

In 1984, conductivity and water temperature at Stations #390 and #393 decreased from the surface to the bottom, reflecting the warm buoyant pulp mill effluent being discharged to the surface. In 1985, these profiles were reversed, implying the influence of the newly installed mill diffuser discharging the effluent to the bottom rather than the surface. The actual variations in conductivity and water temperature were small, with conductivity varying within 15 umhos/cm and temperature within 1°C.

Station #402 was probably influenced by the WPCP effluent discharging from its submerged diffuser outfall, as the profiles for both years indicate higher conductivity and water temperature at the lake bottom than at the surface. The magnitude of variation in conductivity was higher at this station than at stations #390 and #393, varying by 35 umhos/cm in 1984.

3.2.3 Diffuser Profiles

Profiles were taken over the submerged diffuser outfall for the mill at three locations - at the end of the diffuser pipe (Station #439), 100 feet from the pipe end (Station #440), and 200 feet from the pipe end (at the first diffuser port) (Station #441). A summary of the all diffuser profile data is contained in Appendix B.



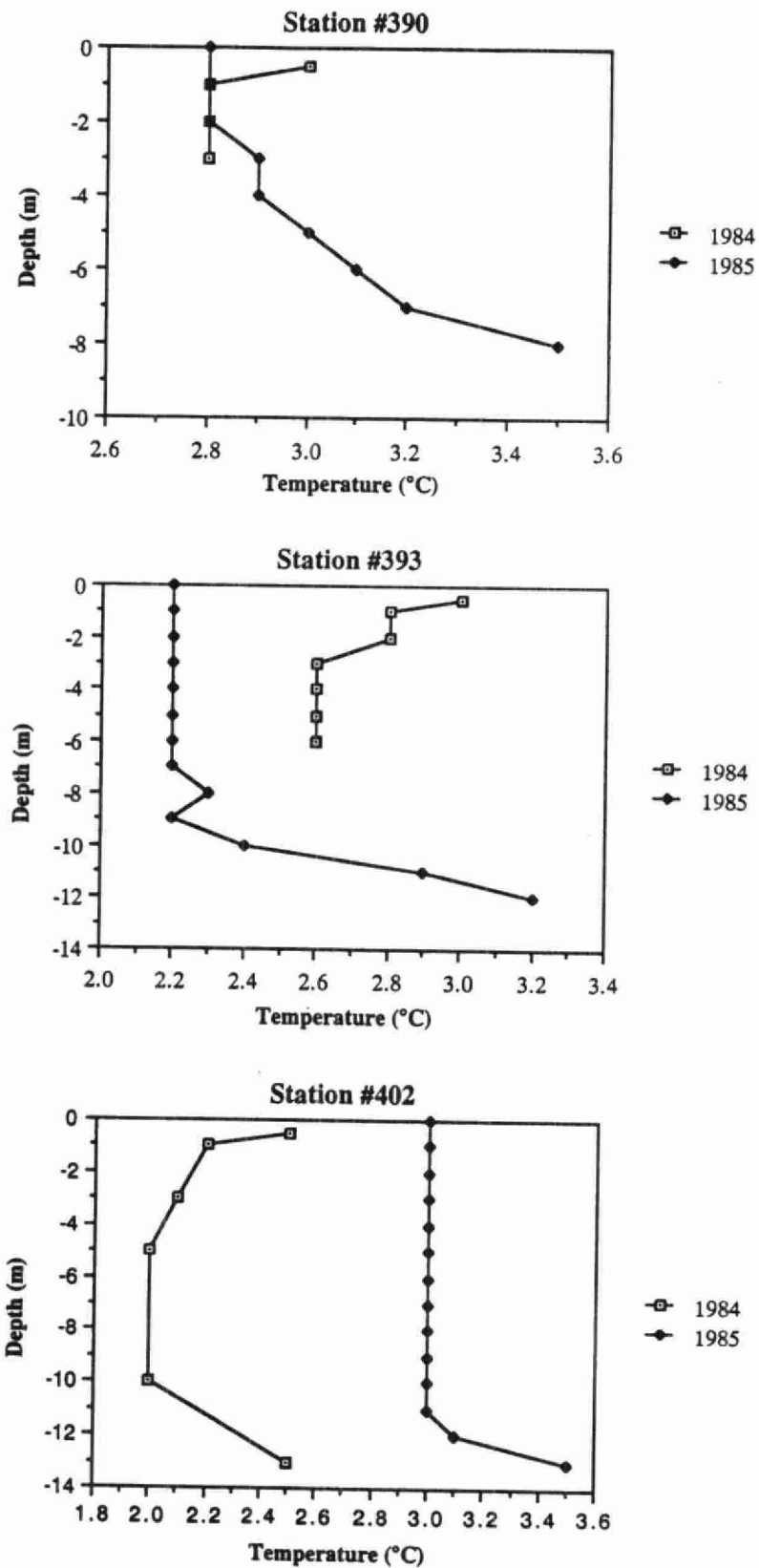


Figure 7. Depth profiles of water temperature at Stations #390, #393, and #402 in 1984 and 1985.

Most parameters exhibited a distinct dilution profile above the diffuser. Nitrate, however, remained at a relatively constant concentration throughout the water column. This suggests that the presence of nitrate is independent of the mill outfall. The WPCP effluent is the probable source of nitrate in this area. Other parameters, such as aluminum, iron, DOC, ammonia, and total phosphorous, have widely varying bottom to surface ratios between stations on the diffuser. This is primarily attributable to the variation in concentration at the diffuser (bottom sample) at each station. In general, concentrations at the diffuser tend to decrease from the first to last port.

The diffuser profile samples were collected between 10:54 and 12:18 on May 21, 1985. During this period, the winds were light and from the southwest. Shortly after noon, the winds increased in velocity and changed direction slightly to southwest by west. To determine the possible effects of a change in plume direction on the diffuser profiles, the profiles were repeated from 13:00 to 14:00 and analyzed for total reactive phenolics only. The profiles for the two time periods at each station are illustrated in Figure 8. Although the bottom samples (on the diffuser) remained at a relatively constant concentration, the surface samples at the later sampling period are less dilute. It appears that the increased wind speed in the afternoon was forcing the plume back towards the outfall and inhibiting dilution. The magnitude of the change in dilution is reflected in the bottom to surface ratios. The column dilution ratios decreased by a factor of 2 at the nearshore pipe station up to a factor of 15 at the far end of the pipe. These ratios only reflect the dilution in the water column directly above the diffuser, and are not to be confused with the design dilution ratio of 25:1 for the diffuser. It is impossible to calculate this dilution ratio because there is no concurrent information on plume speed and direction.

3.2.4 Water Quality Characteristics

A summary of all water quality data from the 1984 and 1985 surveys is contained in Appendix C. Table 12 summarizes the parameters analyzed, but not detected, and the minimum reportable amount (MRA) for each. The MRA is a detection level concentration determined at the laboratory which incorporates equipment sensitivity and precision, as well as variability associated with sample preparation.

The significance of the values for many of the water quality variables can be assessed, in part, by comparing them to water quality objectives and guidelines. The Ontario Provincial Water Quality Guidelines (PWQO's) are "a set of narrative and numerical criteria designed

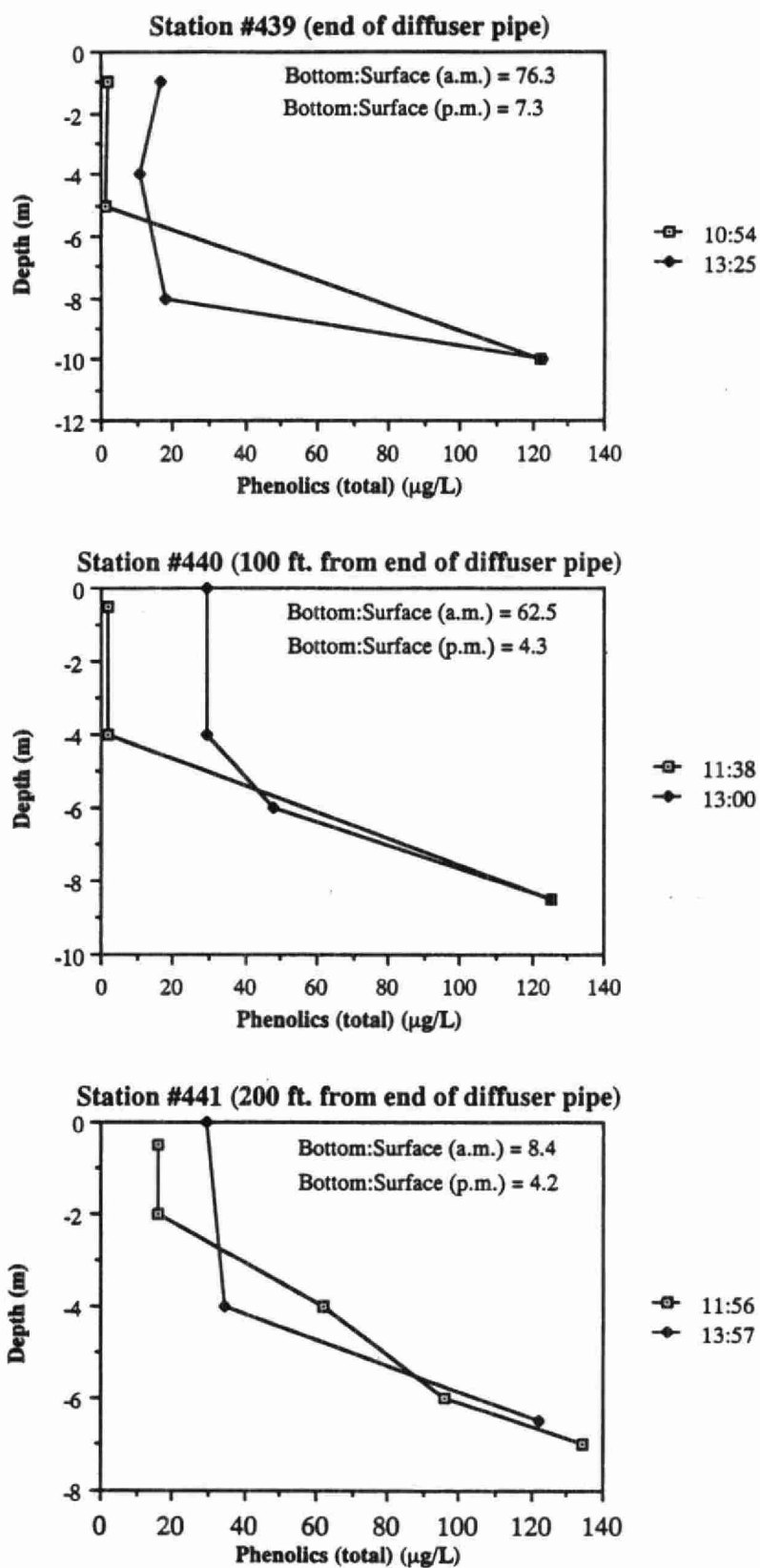


Figure 8. Diffuser profiles for total reactive phenolics at two time periods on May 21, 1985.

Table 12. Analyzed parameters not detected in water samples.

Parameter	Minimum Reportable Amount
Arsenic	0.001 mg/L
Cobalt (analyzed 1984 only)	0.001 mg/L
Selenium (analyzed 1984 only)	0.001 mg/L
Silver (analyzed 1984 only)	0.005 mg/L
Trichloroethylene	1 ug/L
Tetrachloroethylene (analyzed 1984 only)	1 ug/L
Chlorodibromoethane	N/A
Dichlorobromoethane	1 ug/L
Hexachloroethane	1 ng/L
Octachlorostyrene	1 ng/L
Hexachlorobutadiene	1 ng/L
1,2,3-trichlorobenzene	5 ng/L
1,2,4-trichlorobenzene	5 ng/L
1,3,5-trichlorobenzene	5 ng/L
1,2,3,4-tetrachlorobenzene	1 ng/L
1,2,3,5-tetrachlorobenzene	1 ng/L
1,2,4,5-tetrachlorobenzene	1 ng/L
Pentachlorobenzene	1 ng/L
Hexachlorobenzene	1 ng/L
2,3,6-trichlorotoluene	5 ng/L
2,4,5-trichlorotoluene	5 ng/L
2,6,A-trichlorotoluene	5 ng/L
p-cresol	N/A
2,5-xyleneol	N/A
Chloro-p-cresol	N/A
2-chlorophenol	N/A
4-chlorophenol	N/A
2,4-dichlorophenol	N/A
2,3,4-trichlorophenol	N/A
2,3,4-trichlorophenol (*)	100 ng/L
2,4,5-trichlorophenol	N/A
2,4,5-trichlorophenol (*)	50 ng/L
2,4,6-trichlorophenol	N/A
2,4,6-trichlorophenol (*)	50 ng/L
2,3,4,5-tetrachlorophenol	N/A
2,3,4,5-tetrachlorophenol (*)	50 ng/L
2,3,5,6-tetrachlorophenol (*)	50 ng/L
2,4,5,6-tetrachlorophenol	N/A
Pentachlorophenol	N/A
Pentachlorophenol (*)	50 ng/L
Acetosyringone	N/A

continued . . .

Table 12. Analyzed parameters not detected in water samples (concluded).

Parameter	Minimum Reportable Amount
Capric Acid	10 ug/L
Lauric Acid (1984 only)	10 ug/L
Myristic Acid (1984 only)	10 ug/L
Palmitic Acid (1984 only)	10 ug/L
Stearic Acid (1984 only)	10 ug/L
Oleic Acid (1984 only)	10 ug/L
Linoleic Acid (1984 only)	10 ug/L
Arachidic Acid (1984 only)	10 ug/L
Pimaric (1984 only)	10 ug/L
Sandaracopimaric Acid (1984 only)	10 ug/L
Levopimaric Acid	10 ug/L
Palustric Acid (1984 only)	10 ug/L
Isopimaric Acid (1984 only)	10 ug/L
Neobietic Acid	10 ug/L
Abietic Acid	10 ug/L
Dehydroabietic Acid (1984 only)	10 ug/L
Benzoic Acid (analyzed 1984 only)	10 ug/L
Salicylic Acid (analyzed 1984 only)	10 ug/L
Phthalic Acid (analyzed 1984 only)	10 ug/L
Aldrin	1 ng/L
beta-BHC	1 ng/L
alpha-chlordane	2 ng/L
gamma-chlordane	2 ng/L
Dieldrin	2 ng/L
Methoxychlor	5 ng/L
Endrin	4 ng/L
Endosulfan-sulphate	4 ng/L
Endosulfan I	2 ng/L
Endosulfan II	4 ng/L
Heptachlorepoxyde	1 ng/L
Heptachlor	1 ng/L
Mirex	5 ng/L
Oxychlordane	2 ng/L
OP-DDT	5 ng/L
PCP (total)	20 ng/L
PP-DDD	5 ng/L
PP-DDE	1 ng/L
PP-DDT	5 ng/L
Dicamba	100 ng/L
Picloram	100 ng/L
Silvex	50 ng/L
2,4-D	100 ng/L
2,4-DB	200 ng/L
2,4-DP	100 ng/L
2,4,5-T	50 ng/L

N/A Minimum Reportable Amount not available.

(*) Test done by Drinking Water Lab, as opposed to Trace Organics Lab

for the protection of aquatic life and recreation in and on the water" (OMOE 1984). The Great Lakes Water Quality Agreement objectives (GLWQA) are "based on available information on cause/effect relationships between pollutants and receptors to protect the recognized most sensitive use in all waters" (International Joint Commission 1987). The water quality guidelines proposed by the Canadian Council of Resource and Environment Ministers (CCREM) are the numerical criteria recommended to support and maintain aquatic life. These guidelines were developed to provide basic scientific information about the effects of water quality parameters on uses in order to assess water quality issues and concerns and to establish water quality objectives for specific sites (Canadian Council of Resource and Environment Ministers 1987). Although similar, there are some differences between the three numerical objectives/guidelines.

Tables 13 and 14 summarize the results for metals and all other parameters, respectively, for which objectives/guidelines are available. The data are summarized with respect to station locations of samples in non-compliance with these objectives and guidelines. For the purpose of this report, non-compliance at a specific station indicates that at least one sample from this station exceeded the objective. Other samples taken in the same year may be lower than the objective (see complete data set in Appendix C).

A two-way Analysis of Variance (ANOVA) procedure was used to compare the water quality data between 1984 and 1985. This analysis allows for the separation of the effects of year and station location. As this was not a completely balanced study (i.e. the number of analyses at each station were not the same), a Type III Sums of Squares procedure was used (SAS Institute Inc. 1988). The data were log transformed to minimize the data variability. Normal distribution plots of the data before and after this transformation indicated that the assumption of normality was more closely met with the transformed data. All values reported at the minimum reportable amount were precluded from the analyses. The ANOVA results are summarized in Table 15 for all parameters for which there was sufficient data.

General water quality observations, non-compliance with water quality objectives, and pre- and post-diffuser comparisons are discussed by parameter group in the following sections.

Table 13. Summary of stations in non-compliance with water quality objectives for metals. (PWQO - Ontario Provincial Water Quality Objectives, GLWQA - Great Lakes Water Quality Agreement, CCREM - Canadian Council of Resource and Environment Ministers (Environment Canada)).

Parameter	Objective	Agency	Stations in Non-Compliance with Objective	
			1984	1985
Aluminum	75 ug/L(1)	PWQO, CCREM	none	381, 383, 396, 407, 417
Arsenic	100 ug/L	PWQO	none (2)	none (2)
	50 ug/L	GLWQA, CCREM	none (2)	none (2)
Cadmium	0.2 ug/L	PWQO, GLWQA, CCREM	380 (3)	393, 396, 404, 407 (3)
Chromium	100 ug/L	PWQO	none	not analyzed
	50 ug/L	GLWQA	none	not analyzed
	2.0 ug/L	CCREM	387, 400, 406, 408, 416	not analyzed
Copper	5 ug/L	PWQO, GLWQA	none	not analyzed
	2 ug/L	CCREM	391, 403	not analyzed
Iron	300 ug/L (4)	PWQO, GLWQA, CCREM	none	396, 407
Lead	20 ug/L	PWQO, GLWQA	387	376, 407
	1 ug/L (4)	CCREM	387 (5)	376, 383, 393, 396, 407 (5)
Mercury	0.2 ug/L	PWQO, GLWQA	383 (?), 417	none
	0.1 ug/L	CCREM	383 (?), 391, 417	383
Nickel	25 ug/L	PWQO, GLWQA, CCREM	none	not analyzed
Selenium	100 ug/L	PWQO	none (6)	not analyzed
	10 ug/L	GLWQA	none (6)	not analyzed
	1 ug/L	CCREM	none (6)	not analyzed
Silver	0.1 ug/L	PWQO, CCREM	N/A (7)	not analyzed
Zinc	30 ug/L	PWQO, GLWQA, CCREM	387	376, 383, 393, 396, 407, 408, 409

(1) Based on a pH of >6.5 to 9.0

(2) All concentrations less than the Minimum Reportable Amount (MRA) of 0.001 mg/L (1 ug/L).

(3) MRA of 0.0003 mg/L (0.3 ug/L) is greater than the objective: stations listed are those which exceed the MRA.

(4) Based on an alkalinity of 40 mg/L as CaCO₃ (Kinkead and Chatterjee 1974).

(5) MRA of 3 ug/L (sometimes reported in 1985 as 1 ug/L?) is greater than the objective: stations listed are those which exceed the MRA.

(6) All concentrations less than the MRA of 0.001 mg/L (1 ug/L).

(7) MRA of 0.005 mg/L (5 ug/L) is greater than the objective. All concentrations less than the MRA.

Table 14. Summary of stations in non-compliance with water quality objectives for compounds other than metals. (PWQO - Ontario Provincial Water Quality Objectives, GLWQA - Great Lakes Water Quality Agreement, CCREM - Canadian Council of Resource and Environment Ministers (Environment Canada)).

Parameter	Objective	Agency	Stations in Non-Compliance with Objective	
			1984	1985
Nutrients:				
Ammonia	15.4 mg/L(1)	PWQO	none	none
	2.4 mg/L(1)	CCREM	none	none
Nitrite	0.06 mg/L	CCREM	none	none
Phosphorous	20 ug/L	PWQO	391	385, 395, 399, 403, 404, 409, 413, 425
Microbiological:				
Total coliforms	1000 cnt/100 mL	PWQO	none	none
Fecal coliforms	100 cnt/100 mL	PWQO	none	none
Organics:				
Dissolved Oxygen	8.0 mg/L (2)	PWQO	none	393
	6.0 mg/L	GLWQA	none	none
	6.5 - 9.5 mg/L	CCREM	none	none
Phenols (total)	1.0 ug/L	PWQO, GLWQA	368, 369, 370 ,372, 373, 375, 376, 377, 379, 380, 381, 382, 383, 384, 386, 389, 390, 391, 392, 393, 394, 385, 386, 401, 402, 403, 404, 407, 408, 409, 417	370, 371, 372, 373, 375, 376, 377, 379, 380, 381, 383, 384, 385, 386, 388, 389, 390, 391, 392, 393, 394, 395, 396, 399, 401, 402, 403, 404, 406, 407, 408, 409, 411, 412, 413, 415, 417, 418, 421, 425, 426, 428
alpha-BHC	0.01 ug/L	PWQO, CCREM	none	383, 404, 407, 408
Resin Acids:				
Dehydro-abietic Acid	12.0 ug/L (pH=7.5)	PWQO	none	404
Total Resin Acids	33 ug/L (ph=7.5)	PWQO	none	404

(1) Based on un-ionized ammonia concentration at pH of 7.2, temperature of 5oC.

(2) Based on 54% saturation required for cold water biota at an average temperature of less than 5oC.

Table 15. Summary of two-way Analysis of Variance (ANOVA) results for selected water quality parameters.

Parameter	No. of Stations	Significant Difference between Stations	Significant Difference between Years	Significant Interaction between Station & Year	No. of Stations
Colour (apparent)	27	No	No	No	26
Conductivity (25oC)	52	No	Yes	No	51
Conductivity (ambient)	26	No	No	No	25
Temperature	24	No	Yes	No	23
Total Dissolved Solids	21	No	Yes	No	20
Total Suspended Solids	32	No	Yes	No	31
Turbidity	52	Yes	Yes	No	51
Chloride	19	Yes	No	No	18
pH	27	Yes	Yes	Yes	26
Sodium	43	Yes	Yes	No	42
Sulphate	38	No	No	No	37
Aluminum	21	No	No	No	20
Barium	21	No	No	No	20
Iron	20	No	Yes	No	19
Lead	21	No	No	No	20
Zinc	11	No	No	No	10
Ammonia	20	No	Yes	No	19
Nitrate	32	No	Yes	No	31
Phosphorous	31	No	No	No	30
BOD5	27	Yes	Yes	No	26
COD	3	No	Yes	No	2
Dissolved Oxygen	50	Yes	Yes	Yes	49
Dissolved Organic Carbon	38	Yes	Yes	Yes	37
Phenolics (total)	44	Yes	Yes	No	43

3.2.4.1 Physical and Inorganic Parameters

Apparent colour is used for the assessment of industrial wastewaters, such as pulp and paper mills, where colour is usually contributed by colloidal or suspended material. Apparent colour values were high in 1984 at Stations #391 (17 HZU), #395 (17 HZU), #396 (15, 12, and 12 HZU), #402 (47 HZU), #403 (24 HZU), and #404 (22 HZU). These stations are adjacent to the pulp mill main outfall. In 1985, high colour values were noted only at Stations #395 (10 HZU) and #404 (12 HZU). There was no significant difference in apparent colour values between 1984 and 1985.

Conductivity, measured at 25°C, was similar in Jellicoe Cove and Lake Superior. In 1984, elevated values were found near the main mill outfall at Stations #390 (216 umhos/cm), #391 (211 umhos/cm) and #402 (131 umhos/cm). These high values were not noted in 1985. Conductivity decreased significantly from 1984 to 1985.

The variability of ambient air temperature during May makes it difficult to compare surface water temperatures between years. In addition, temperature was only recorded at a limited number of stations in Lake Superior in 1985. However, some general trends are evident. In 1984, maximum temperatures were noted immediately adjacent to the main mill outfall, with progressively cooler temperatures at the stations extending out into the lake. In 1985, higher temperatures were found over a much larger area, implying that the increased diffusion is dispersing the warmer effluent more effectively. A significant increase in temperature from 1984 to 1985 supports this supposition.

Elevated solids concentrations were historically documented as an impact to the study area. TDS concentrations of 190 to 340 mg/L and TSS concentrations of 5 to 50 mg/L were found within a 350 meter range of the main mill discharge in 1969 (OMOE 1972). Solids were generally much lower in 1984 and 1985; TDS values were usually less than 100 mg/L and TSS less than 5 mg/L in both years. Elevated levels were noted in four samples in 1984 only at Stations #389 (TSS = 7 mg/L), #391 (TDS = 155 mg/L, TSS = 15 mg/L), #400 (TSS = 9 mg/L) and #401 (TSS = 70 mg/L). There was no significant difference between stations for either TDS or TSS, indicating there is no discernible point source gradient from the mill or WPCP discharge. There was a significant decrease in TDS and TSS concentrations between 1984 and 1985.

A significant increase in turbidity from 1984 to 1985 probably reflects the increase in this parameter in the mill effluent. Turbidity was highest at Station #401 in 1984 (7.6 FTU). This high value is probably related to the high suspended solids concentration in this station sample. In 1985, the highest turbidity was recorded at Station #390 (6.4 FTU). A significant difference between station turbidity values further confirms that the mill outfall is the primary source of turbidity.

Sodium can be effectively used as a tracer of pulp mill effluents because of the elevated concentrations usually present in the effluent. As expected, there were significant station differences in sodium concentrations in 1984 and 1985, confirming a definite point source of this compound. There was also a significant decrease in concentrations between 1984 and 1985, probably attributable to both the increased dilution of the effluent through the diffuser outfall and the significant decrease in sodium levels in the mill effluent. The two highest sodium concentrations were recorded in 1984, at Stations #390 (23.00 mg/L) and #391 (24.00 mg/L).

Contour mapping of sodium concentrations on each sampling date effectively illustrates both the variability of the plume and reduction in localized sodium levels resulting from increased initial dilution of the effluent. Figures 9 and 10 show the sodium concentrations on the three days of the 1984 sampling and the two days of the 1985 sampling, respectively. The influence of wind direction on the configuration and areal extent of the effluent plume is evident. These figures also illustrate the extreme and rapid changes in surface water concentrations that can result from changes in the plume. On May 16, 1984 the prevailing winds were from the northwest, resulting in a plume extending southeast along the shoreline of Lake Superior. On May 19 and 20, 1984 the prevailing winds were from the east to southeast, concentrating the plume at the outfall, and driving it around the Peninsula into Jellicoe Cove. Similar patterns are evident on May 14 and May 17, 1985. Figures 9 and 10 also show the effects of increased effluent diffusion in 1985, as the plume concentrations are more dilute than reported for 1984.

Chloride concentrations also exhibited a significant difference between stations. Levels were generally less than 2.0 mg/L, with slightly elevated values of 3.0 to 4.0 mg/L found near the pulp mill and WPCP discharges. A single high value of 20.0 mg/L was found at Station #391 in 1984. There was no significant decrease in chloride concentrations between 1984 and 1985.

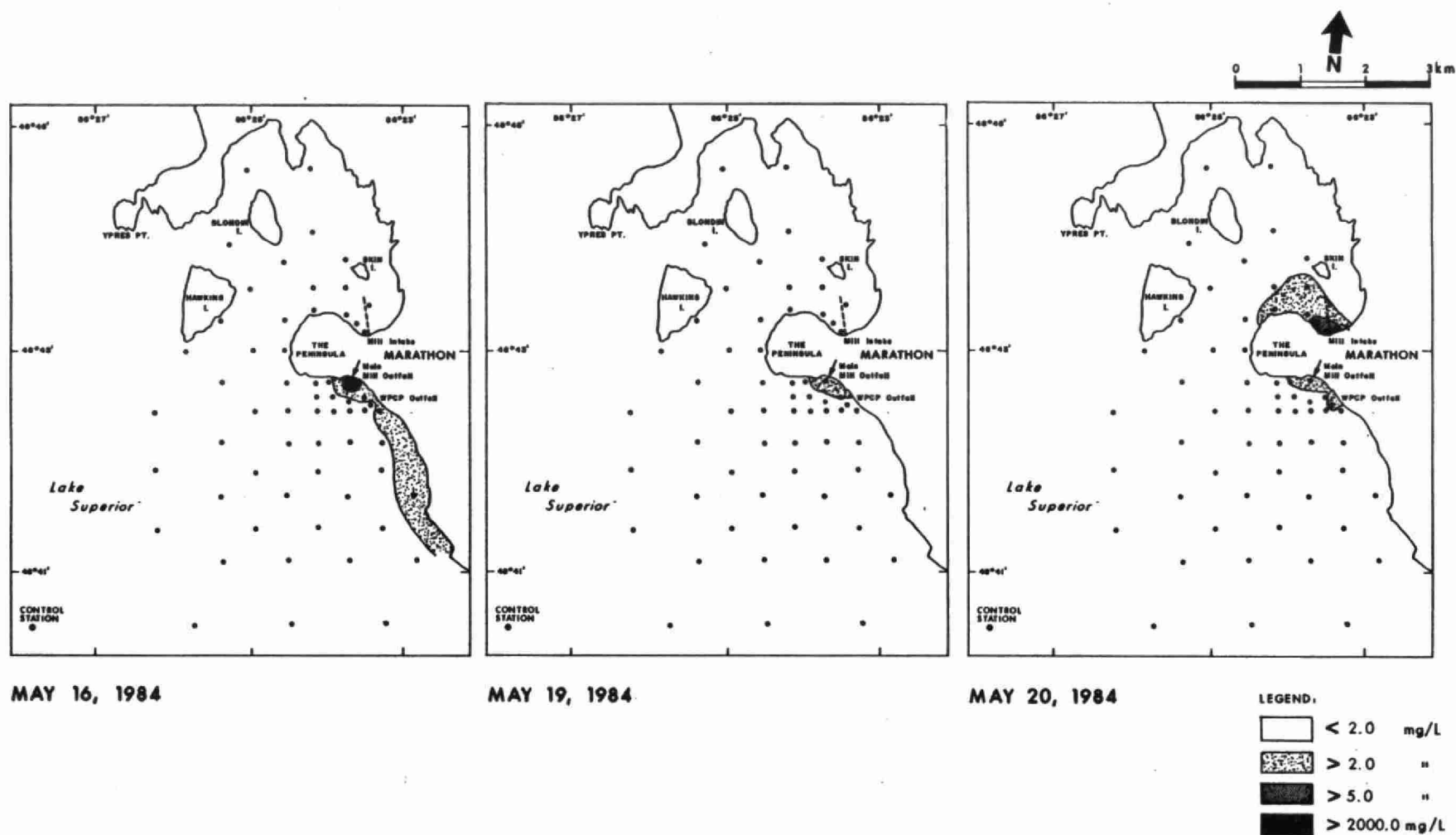


Figure 9. Sodium concentrations on each sampling day in 1984.

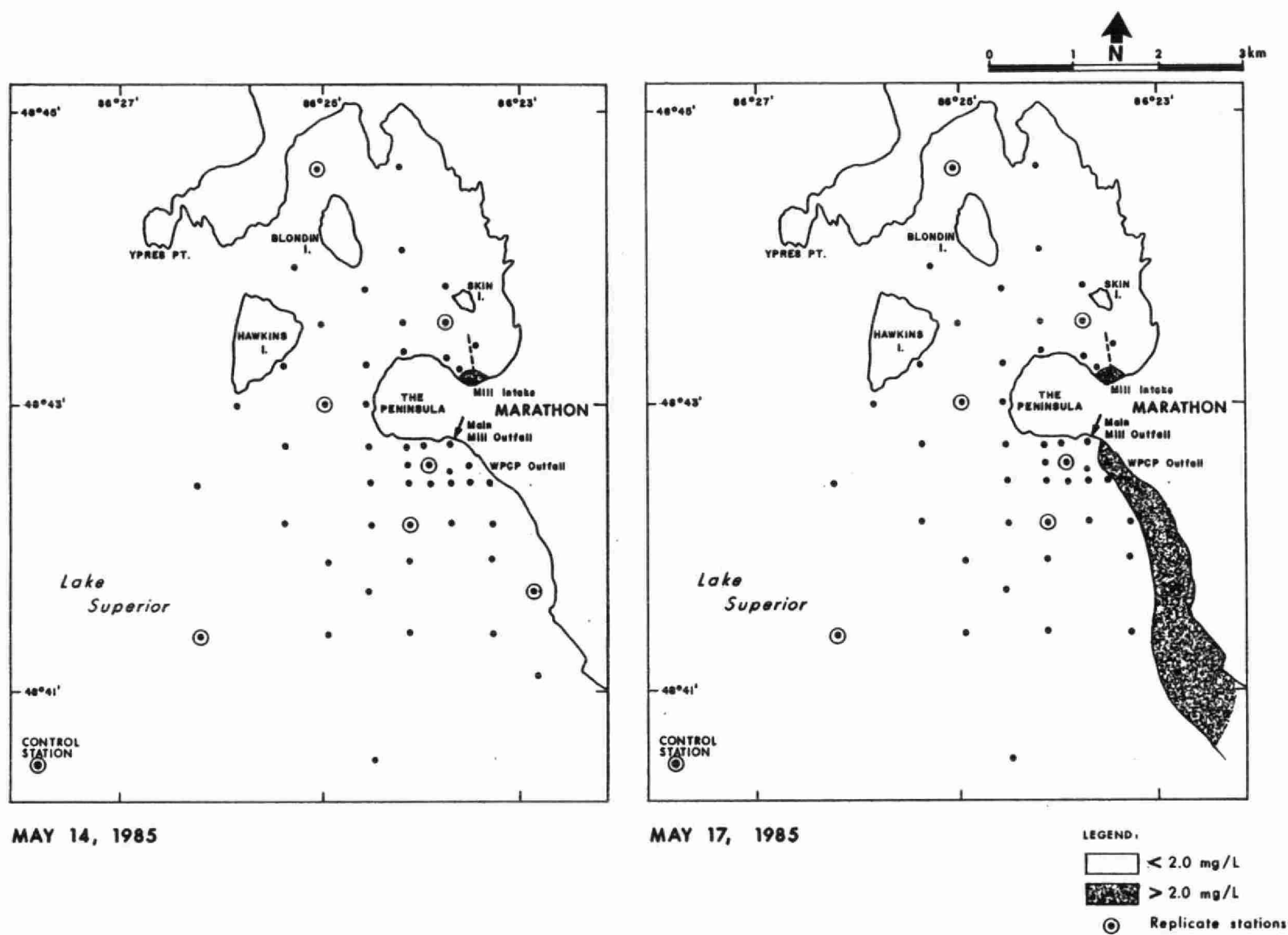


Figure 10. Sodium concentrations on each sampling day in 1985.

In 1984, pH values ranged from 6.8 to 8.4, with a mean value of 7.5 (n = 173). In 1985, the range was from 6.7 to 7.7, with a mean of 7.1 (n = 49). There was no discernible pattern to pH variation in the harbour or Lake Superior. Although the ANOVA procedure showed significant differences between stations and years, this cannot be meaningfully interpreted because of the significant interaction between the two factors (Table 15).

Sulphate values were similar in Jellicoe Cove and open Lake Superior in both years. There was no significant difference between stations or between years. A single high value of 65.25 mg/L was again recorded at Station #391 in 1984 only. As this station is directly adjacent to the main mill outfall, the abnormally high values for chloride, sodium and sulphate in this sample may represent an isolated slug of concentrated wastewater.

3.2.4.2 Metals

Metals concentrations in water samples were generally low, with some station samples exceeding the PWQO's by a moderate amount. Of the metals for which an ANOVA could be performed, only iron showed a significant difference between years, increasing from 1984 to 1985. There were no significant station differences for any metals.

Aluminum concentrations did not exceed the objective of 75 µg/L (for pH > 6.5 to 9.0) at any stations in 1984. In 1985, the objective was exceeded at five stations - two near the mill sump overflow in Jellicoe Cove and three in Lake Superior. Concentrations in excess of the objective ranged from 110 µg/L to 1600 µg/L (at the mill outfall).

Arsenic was not detected in any water samples in either year. Barium values were generally low. There is currently no water quality objective or guideline for barium.

Cadmium values were also generally low in both years. As the minimum reportable amount for cadmium of 0.3 µg/L is higher than the water quality objective of 0.2 µg/L, it is difficult to compare the reported concentrations to the objective. However, the minimum reportable amount was exceeded at one station within Jellicoe Cove during 1984, and at four stations near the mill and WPCP outfalls in 1985.

Copper concentrations did not exceed the PWQO of 5 µg/L at any stations in 1984. However, the lower CCREM guideline of 2 µg/L was exceeded at Stations #391 and #403, adjacent to the mill and WPCP outfalls, respectively. Copper was not analyzed in 1985.

Chromium concentrations were very low, and considerably below the PWQO of 100 µg/L in all samples.

Iron exceeded the PWQO of 300 µg/L in 1985 only at Stations #396 (1300 µg/L) and #407 (310 µg/L). Station #396 is directly adjacent to the WPCP outfall. Lead concentrations exceeded the PWQO of 20 µg/L at Station #387 (49 µg/L) in 1984. In 1985, lead exceeded the objective at Stations #376 (3000 µg/L) and #407 (20 µg/L).

In 1984, a single mercury sample exceeded the PWQO of 0.2 µg/L at Station #417 (0.20 µg/L) in Lake Superior. No mercury concentrations exceeded the PWQO in 1985, although samples at Station #383 did exceed the CCREM guideline of 0.1 µg/L by a minor amount. It should be noted that these mercury concentrations reflect only the total elemental mercury present in the water samples. The methylated forms of mercury, particularly methylmercury and dimethylmercury, are of the most concern in the aquatic environment because they have a high affinity for biotic tissues, are readily accumulated by aquatic organisms and tend to bioconcentrate because of rapid uptake and slow depuration.

Nickel, selenium, and silver were analyzed in 1984 only. Nickel did not exceed the PWQO in any samples. Selenium and silver were not detected.

In 1984, zinc exceeded the PWQO of 30 µg/L at Station #387 (280 µg/L). In 1985, the objective was exceeded at Stations #376 (4000 µg/L) and #383 (100 µg/L) in Jellicoe Cove, and Stations #393 (47 µg/L), #396 (73 µg/L), #407 (670 µg/L), #408 (160 µg/L) and #409 (40 µg/L) in Lake Superior.

The particularly high values for lead and zinc at Station #376 are assumed to be from resuspension of metals adsorbed onto fine-grained sediments, as the station is not directly adjacent to any point source discharge. This interpretation is supported by the observation that the May 14, 1985 sample containing the maximum values of lead and zinc also had a high TSS value of 612 mg/L. Most of the other elevated metals concentrations are located in the nearshore, close to the main mill and WPCP outfalls. The high concentrations in these areas are probably due to active source loadings, as there is unlikely to be any resuspension of the adsorbed contaminants primarily associated with the fine-grained sediment in this predominantly sandy, active nearshore environment.

3.2.4.3 Nutrients

The concentrations of ammonia, total Kjeldahl nitrogen (TKN), nitrite, nitrate and phosphorous were generally similar to background levels in both years (as determined from control Station #426). The concentrations of un-ionized ammonia did not exceed the PWQO or the more stringent CCREM guideline in either year. Nitrite did not exceed the CCREM guideline for the protection of aquatic life in either year. Ammonia concentrations decreased significantly from 1984 to 1985, whereas nitrate concentrations increased significantly over this time. This may be due to ammonia nitrification.

In 1984, the total phosphorous concentration exceeded the PWQO for the avoidance of nuisance concentrations of algae in lakes at Station #391 only. In 1985, the objective was exceeded at nine stations in Lake Superior, all in the vicinity of the main mill outfall and the WPCP discharge. The magnitude of the concentrations exceeding the objective was small, ranging from 0.022 to 0.055 µg/L. These findings are not of great concern, given the oligotrophic nature of the study area.

3.2.4.4 Microbiological

Bacterial counts were very low in both 1984 and 1985. *Escherichia coli*, *Pseudomonas aeruginosa*, fecal coliforms and fecal streptococcus were analyzed in 1985 at six stations only. Station #391 in 1984 was the only station with bacterial counts greater than the minimum reportable number of 4 organisms/100 mL, with 10 organisms/100 mL for each of these parameters. Total coliforms were well below the PWQO for recreational water use of 1000 organisms/100 mL in both years.

These counts are considerably reduced from those found in previous surveys. The 1969 water quality survey found that, within 610 meters of the main sump overflow in Jellicoe Cove, two out of the ten sites exceeded 5000 total coliforms/100 mL and seven sites exceeded 1000 coliforms/100 mL. Fecal streptococci densities of up to 572 organisms/100 mL were found in this area. Conditions were also impaired on the Lake Superior side of the Peninsula, where fecal coliform counts of up to 14,600 organisms/100 mL and fecal streptococci counts of up to 920 organisms/100 mL were recorded (OMOE 1972). The low densities of bacterial organisms in both the receiving water and effluents in 1984 and 1985 reflect the decreased bacterial contamination from the mill effluent and the

improvement in effluent quality at the WPCP following the installation of secondary treatment. It is also indicative of good disinfection practice at the WPCP.

The heterotrophic bacteria count is not a test for a specific organism; rather, it is designed to enumerate as large a number as possible of those bacteria in water that require some carbon for their growth (OMOE 1981). Hence, large heterotrophic counts are not necessarily indicative of impaired water quality. Heterotrophic bacteria counts are primarily used to compare general bacteriological quality between areas and/or over time. They can also be used to establish gradients from a point source that might indicate bacteriological contamination. The heterotrophic bacteria levels recorded in 1984 and 1985 do not exhibit any discernible density gradients, supporting the conclusion that previously identified bacteriological contamination problems are no longer evident.

3.2.4.5 Organic Parameters

BOD₅ results were generally below 1.0 mg/L in both years. High values were recorded in 1984 at Stations #391 (24.0 mg/L) (at the mill discharge point), #395 (3.7 mg/L), #401 (2.2 mg/L) and #402 (3.6 mg/L). One elevated value was found in 1985 at Station #396 (7.1 mg/L). These stations are all directly adjacent to the mill outfall. There was a significant decrease in BOD₅ concentrations from 1984 to 1985. There were also significant station differences, indicating that the mill and WPCP are the primary point sources of the oxygen demand.

COD values were elevated in 1984 at Stations #391 (84.0 mg/L) and #395 (23.0 mg/L). In 1985, high values were recorded at Stations #394 (22.0 mg/L), #396 (37.2 mg/L), #403 (23.0 mg/L) and #409 (36.5 mg/L). However, it should be noted that in 1985 the control station, #426, had a COD concentration higher than many other stations (19.5 mg/L). COD was not analyzed at Station #426 in 1984. COD values decreased significantly from 1984 to 1985, despite a concurrent increase in COD in the mill effluent.

It is apparent from the BOD₅ and COD results that a high localized oxygen demand was associated with the point of discharge (Station #391) in 1984. After the instalment of the submerged diffuser outfall, this was no longer evident.

The oxygen demand from the effluent does not appear to be depleting the dissolved oxygen (D.O.) in the receiving environment. Only one sample at Station #393 in 1985 was below

the most stringent objective of 8.0 mg/L in both years. A replicate sample collected at the same time showed a D.O. concentration of 12.60 mg/L. All other D.O. concentrations were greater than 12.0 mg/L. A significant difference in D.O. values between stations and between years is difficult to interpret because of the significant interaction between the two factors (Table 15).

A single elevated dissolved organic carbon (DOC) value of 34.5 mg/L at Station #391 in 1984 is consistent with the earlier observation on localized loadings at the mill discharge. Again, significant differences between stations and years difficult to interpret because of a significant interaction.

Tannins are a plant constituent that may be discharged as a waste during the manufacture of paper pulp. Tannins were analyzed at a limited number of stations near the pulp mill discharge, and were below the MRA at most stations. Detectable concentrations were found in 1984 at Station #391 (6 mg/L), and in 1985 at Stations #404 and #409 (both at 1 mg/L).

3.2.4.6 Resin, Fatty and Aromatic Acids

Resin acids are derived from the natural resins found in the wood of coniferous trees, and are released into receiving waters as "extractives" during the pulp processing (Taylor et al. 1988). Fatty acids are formed from the fats stored in the wood to provide winter food reserves for the tree. These fats are hydrolysed during pulping to form fatty acids. Resin and fatty acids are normally found in association in pulp mill liquors and effluents (Tomlinson 1979), and are significant and primary sources of toxicity in pulp and paper mill effluents (McLeay et al. 1986).

Resin acids were below the detection limit at all stations in 1984, and detected at only one station in 1985. The PWQO for dehydroabietic acid is 8.0 µg/L at a receiving water pH of 7.0, and 12.0 µg/L based on a pH of 7.5. At the lower pH, the objective is less than the MRA of 10 µg/L, making it difficult to assess compliance with the objective. However, dehydroabietic acid was found at 30 µg/L at Station #404 in 1985, thus exceeding the objective at both pH values. Isopimaric acid, neoabietic acid, palustric acid, pimaric acid and sandaracopimaric acid were also detected at this station in 1985 at concentrations of 30 or 35 µg/L. The PWQOs for total resin acids of 25 µg/L (pH=7.0) and 45 µg/L (pH=7.5)

were therefore also exceeded at this station. Station #404 is below both the mill and WPCP outfalls.

Fatty acids were also generally not detected. Again, all fatty acids analyzed except capric acid were detected at Station #404 in 1985 at concentrations ranging from 40 to 70 µg/L. There are currently no PWQO's for fatty acids.

The aromatic acids (benzoic, salicylic and phthalic acid) were not detected at any stations.

3.2.4.7 Organohalides and Organochlorine Pesticides

Of the twenty-three volatile organohalide parameters analyzed, only four were detected on at least one occasion. Chloroform was detected at all 17 stations where it was tested for in 1984. The highest concentrations were found at Stations #388 (56 µg/L), #391 (37 µg/L), #392 (31 µg/L), #402 (28 µg/L), and #403 (26 µg/L). All stations were within the potential plume area of the pulp mill discharge. In 1985, chloroform was detected in 5 of 20 samples (25%), with one high concentration at Station #393 (169 µg/L). This station is close to the main mill outfall. As previously noted, chloroform is a common constituent of kraft pulp mill effluents employing a hypochlorite bleaching stage. Chloroform is not considered to be an important hazard for aquatic ecosystems because it has a low toxicity and a low potential for bioaccumulation in aquatic organisms (Bonser et al. 1988).

Carbon tetrachloride (analyzed in 1984 only) was detected at five of the six stations where it was analyzed, at concentrations ranging from 1 to 15 µg/L. Total trihalomethanes were analyzed in 1985 only, and were detected at 5 of the 20 stations analyzed (25%). One high value of 170 µg/L was recorded at Station #393. Trihalomethanes are common byproducts of the chlorine disinfection process employed at wastewater treatment plants. Although not detected in any samples in 1984, 2,3,6-trichlorotoluene was detected at 16 µg/L at Stations #389 and #408 in 1985.

Of the 28 organochlorine pesticides analyzed for, only three were detected in at least one sample. The most ubiquitous of these was α -BHC (the most soluble isomer of hexachlorocyclohexane), being detected in 93% of the samples at concentrations ranging from 2 to 21 ng/L. This compound cannot be linked to any immediate point source, and has been routinely detected at low concentrations throughout the Great Lakes basin. The

pesticide γ -BHC (lindane) was detected in 11% of the samples at low concentrations of 1 to 3 ng/L. Aldrin was detected in 1984 only at Station #396 (5 ng/L).

3.2.4.8 Phenolics

The PWQO of 1.0 $\mu\text{g/L}$ for total reactive phenolics is designed to protect against the tainting of edible fish flesh. This objective was exceeded at 31 out of 62 stations (50%) in 1984 and at 42 out of 52 stations (81%) in 1985. The maximum concentrations recorded in 1984 were 335.0 $\mu\text{g/L}$ at Station #391 and 112.0 $\mu\text{g/L}$ at Station #390. These stations are both located at the mill discharge. The maximum concentration in 1985 was 14.0 $\mu\text{g/L}$ at Station #418. The concentration of total reactive phenolics decreased significantly from 1984 to 1985. There was also a significant station difference, indicating a defined point source discharge.

Contour mapping of reactive phenolics concentrations on each sampling date shows the difference between years in the areal extent of the contamination, and the reduction in localized concentrations resulting from the increased dilution of the diffused effluent (Figures 11 and 12). These maps also serve to again illustrate the influence of wind direction on the configuration and size of the surface plume.

The various substituted phenols measured by the reactive phenolics test differ greatly in potential to impart taste and odour to fish and water. Therefore, these values are not directly interpretable in terms of organoleptic or toxic effects. Despite the number of stations exceeding the objective, there have been no recent reports of fish tainting in this area.

More precise information is obtained from the analyses of phenol and selected substituted phenolic compounds. Chlorinated and speciated phenolic compounds have also been identified as major contributors to the toxicity of pulp mill effluents (McLeay et al. 1986). None of the ten chlorophenolic compounds analyzed were detected in either 1984 or 1985 at any stations. However, five of the nine speciated phenolic compounds were detected in at least one sample.

Phenol was detected in 1985 only in 12 out of 36 samples (33%). Elevated concentrations were found at Stations #391 (48 ng/L) and #403 (157 ng/L). Vanillin was detected at Station #391 (1 $\mu\text{g/L}$) only in 1984. In 1985, vanillin was detected in 25 out of 36 samples

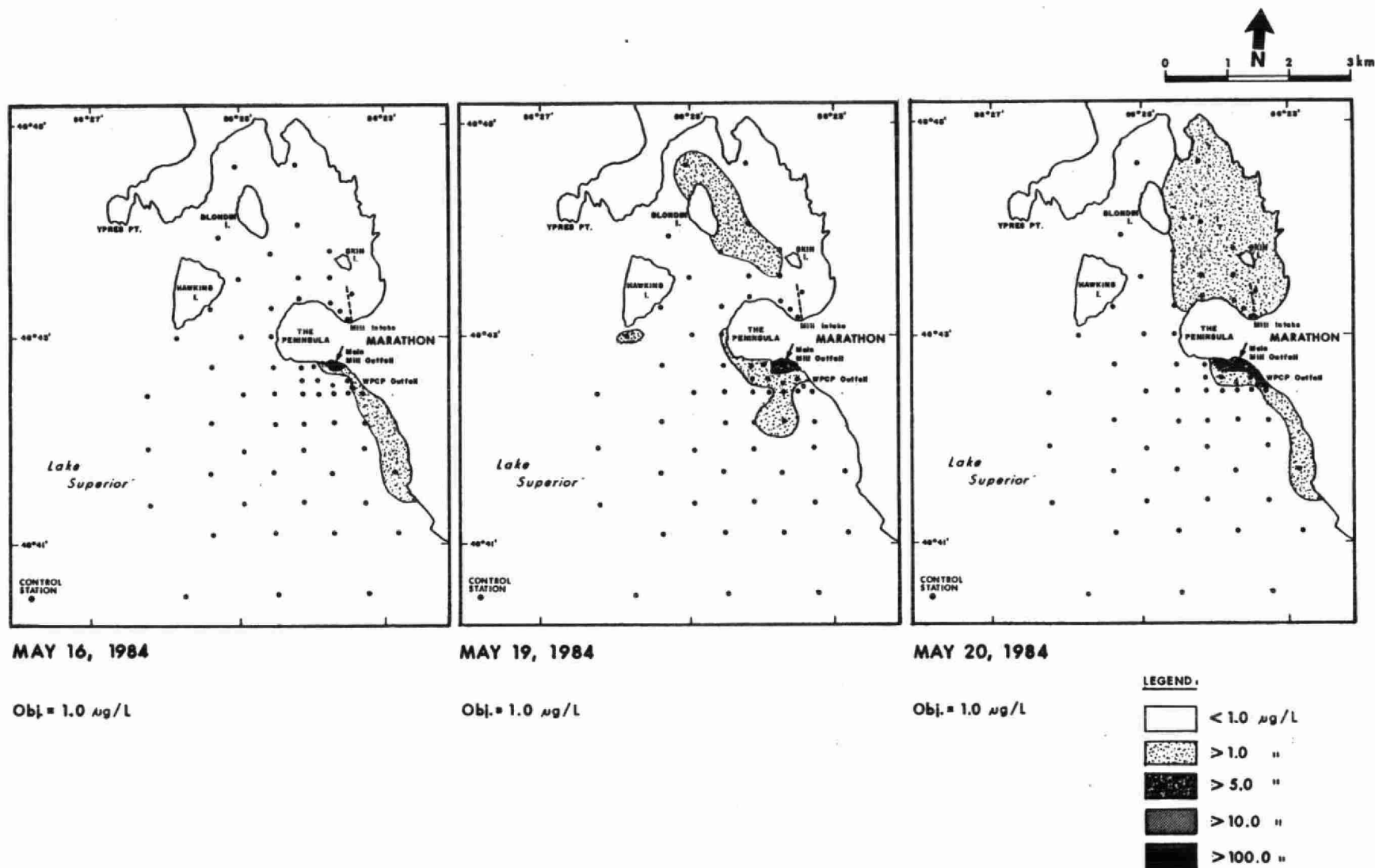


Figure 11. Reactive phenolics concentrations on each sampling day in 1984.

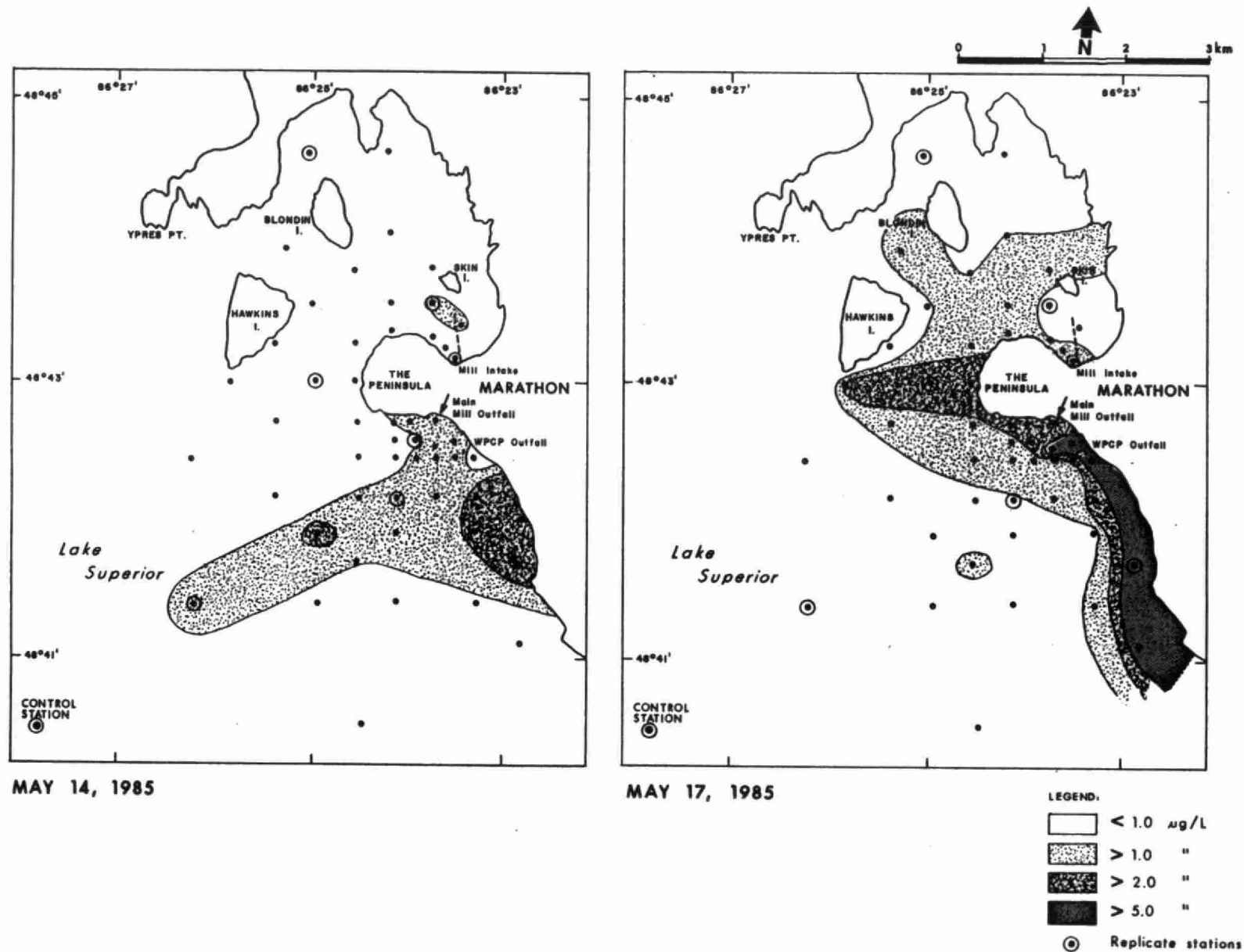


Figure 12. Reactive phenolics concentrations on each sampling day in 1985.

(69%), at concentrations ranging from 7 to 1157 ng/L. The highest concentrations were noted at Stations #395 (394 ng/L), #403 (438 ng/L) and #404 (1157 ng/L). Homovanillic acid was detected in 1985 only in 7 out of 36 samples (19%), at concentrations ranging from 5 to 39 ng/L.

Guaiacol was also detected at Station #391 only in 1984 at a concentration of 2 µg/L. In 1985, guaiacol was detected at 19 out of 36 samples (53%), at concentrations ranging from 7 to 5125 ng/L. The highest concentrations were noted at Stations #393 (1813 ng/L), #395 (1739 ng/L), #403 (1500 ng/L), and #404 (5125 ng/L).

Acetovanillon was not detected in 1984, but was detected at 26 out of 36 samples (72%) in 1985. Concentrations in 1985 ranged from 5 to 939 ng/L, with the highest values recorded at Stations #395 (313 ng/L), #403 (375 ng/L) and #404 (938 ng/L).

Speciated phenolics samples were collected at 18 stations on May 14, 1985 and again on May 17, 1985. The variable nature of the presence of speciated phenolics at a given station is illustrated by the difference in concentrations each day. For example, guaiacol was not detected at Station #404 on May 14, yet had a very high concentration of 1157 ng/L on May 17. This is probably partly attributable to the extreme variability of the plume. The differences may also be due to the variability in analytical precision. Replicate analyses done at Station #393 often showed very different results: guaiacol concentrations for successive replicate samples taken on May 14, 1985 were 1813 and 23 ng/L.

A change in laboratory detection capabilities and reporting units from 1984 to 1985 precluded any statistical comparison of the results between the two years. In addition, because the 1985 results were reported in ng/L rather than the µg/L used in 1984, it may erroneously appear that these compounds were more frequently detected in 1985. However, in trying to compare the two years, it should be noted that most 1985 concentrations were below 1000 ng/L or 1 µg/L.

3.3 SEDIMENT QUALITY

The sediment quality data from the 1984 survey is summarized in the tables in Appendix D. As previously stated, a single grab sample was taken at each station, thus precluding any determination of possible variability or sampling/analytical errors in the values reported.

There are currently no approved sediment quality guidelines for the evaluation of bulk sediment chemistry data. The only existing guidelines are the criteria for assessing the suitability of dredged material for open water disposal. These Open Water Disposal Guidelines (OWDG) are commonly used as a general reference for sediment contamination (Persaud and Wilkins 1976). Table 16 summarizes these guidelines and the stations exceeding them for all parameters covered under these guidelines.

3.3.1 Physical Parameters

Figure 13 shows the grain size composition of sediments in the study area, based on the % fine particle size (silt and clay) at each station. On the basis of the analytical method employed (Microtrac Analyzer), particle size is defined here as sand (> 0.0625 mm), silt (0.0050 to 0.0625 mm), and clay (< 0.0050 mm).

Most of the finer sediments were found in the deeper depositional waters offshore. Sandy coarse sediment composed of small smoothed pebbles was characteristic of the dynamic nearshore zone in Lake Superior. Strong wave action induced by winds makes this zone very active, with continuous transport of any fine-grained material delivered to the nearshore. The harbour sediments were primarily composed of coarse sand.

3.3.2 Metals

Cadmium, cobalt, lead and zinc were not detected at concentrations greater than the OWDG (Table 16) at any station. Chromium and iron concentrations exceeded the OWDG maximum concentration in virtually all samples. Copper concentrations exceeded the guideline at 13 of the 42 stations (30%). Nickel concentrations only occasionally exceeded the guideline (3 of 42 stations, or 7%).

Mercury concentrations in sediments are of particular concern in this area because of residual deposits from the former chlor-alkali plant discharges. Figure 14 shows the spatial distribution of mercury in the sediments. Twenty-two of the 42 stations (52%) exceeded the OWDG of $0.3 \mu\text{g/g}$. The highest concentration of $8.80 \mu\text{g/g}$ was found at Station #393, opposite the mill sump overflow at the site of the former chlor-alkali plant discharge in Jellicoe Cove. High concentrations were also noted just west of this site at Stations #1159 ($7.20 \mu\text{g/g}$) and #1149 ($5.10 \mu\text{g/g}$); between Blondin and Hawkins Islands at Station #592 ($4.40 \mu\text{g/g}$); and south of Hawkins Island at Stations #384 ($4.80 \mu\text{g/g}$) and

Table 16. Summary of non-compliance with OMOE guidelines for open-water disposal of dredge spoils.

Parameter	Guideline Concentration (dry weight)	Stations Exceeding Guideline
Cadmium	1.0 ug/g	none
Chromium	25 ug/g	all except 369
Cobalt	50 ug/g	none
Copper	25 ug/g	384, 387, 397, 398, 406, 411, 418, 422, 428, 436, 437, 592, 594
Iron	10,000 ug/g	all except 383 and 395
Lead	50 ug/g	none
Mercury	0.3 ug/g	372, 378, 379, 383, 384, 385, 387, 397, 398, 406, 411, 418, 422, 428, 433, 436, 437, 592, 594, 1148, 1149, 1159
Nickel	25 ug/g	418, 436, 593
Zinc	100 ug/g	none
Phosphorous (total)	1.0 mg/g	422
Loss on Ignition (600oC)	6%	383, 594, 1159
Solvent Extractables	1.5 mg/g	369, 382, 395, 594, 1148, 1159
PCB's (total)	50 ng/g	22, 372, 378, 382, 385, 387, 397, 411, 418, 592, 1148, 1159

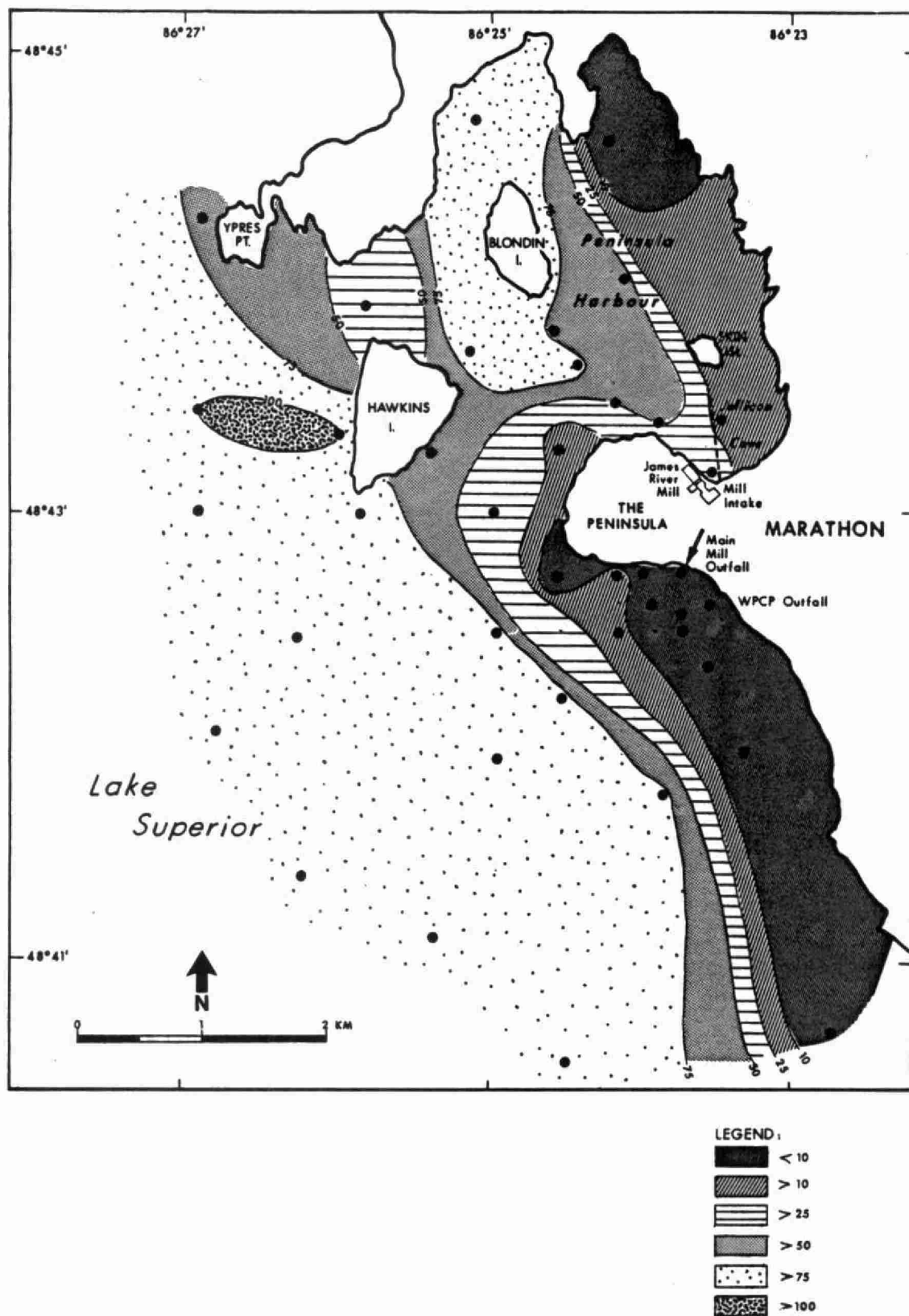
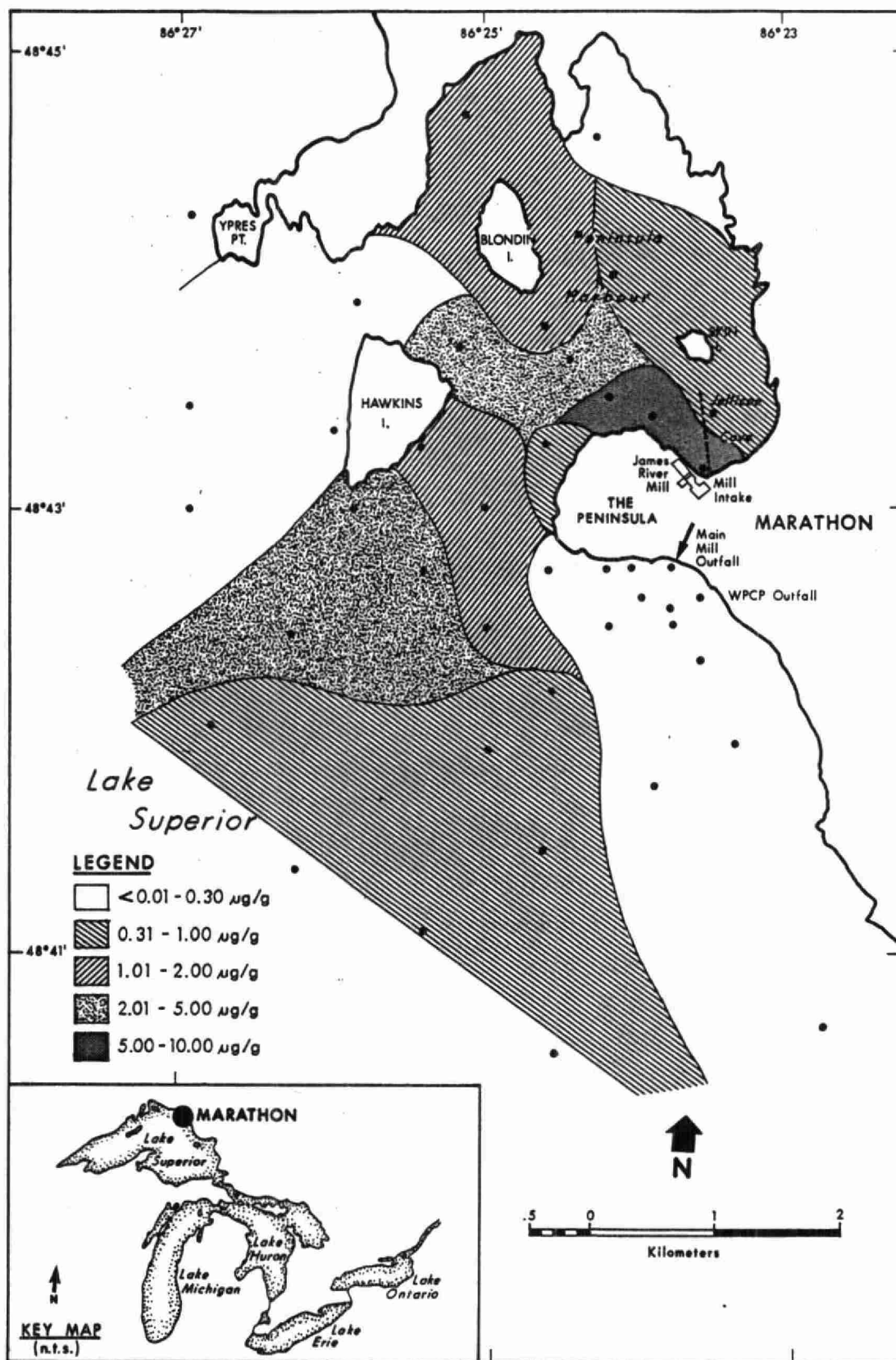


Figure 13. Percent fine particle size (silt and clay) on each sampling day in 1984.



(Open Water Disposal Guideline = $0.30 \mu\text{g/g}$)

Figure 14. Mercury concentrations in sediments collected in 1984.

#397 (3.40 µg/g). Although still well above the OWDG, these concentrations are considerably reduced from those found in previous studies. The maximum sediment mercury concentrations in Jellicoe Cove, near the main mill sump overflow, were recorded at 96.0 µg/g in 1969 (OMOE 1972), 112 µg/g in 1976 (OMOE 1978), and 27.0 µg/g (OMOE unpublished data) in 1983. The reduced concentrations in 1983 and 1984 reflect the cessation of mercury discharge with the closing of the chlor-alkali plant in 1977 and the deposition of cleaner sediments over the contaminated areas since that time. In addition, the distribution of elevated levels over a wider area than previously recorded suggests migration of the mercury from the original source into deeper depositional areas. The full extent of this migration cannot be determined from the limited station sampling grid used in this survey.

Overall, spatial distribution of the various metals generally reflects the sorting of fine-grained material toward the deeper parts of the study area. Forstner and Wittmann (1983) have established the relationship between bulk sediment chemistry and particle size, particularly for metals. The observed similarity in pattern between grain size and chemistry data suggests that at least some of the variation between stations is attributable to grain size effects. Linear correlations between bulk chemistry data and grain size indicators (defined as % particles <63 µm, or combined percentages of silt and clay) show significant correlations for all metals except mercury and chromium (Table 17). This relationship implies that metals concentrations at any given station are a function of both its proximity to a source and the local depositional environment prior to sampling. The lack of correlation between particle size and mercury concentrations suggests that the presence of mercury in the sediments is primarily influenced by proximity to the contaminant source.

To minimize the relative differences in concentrations attributable to differences in depositional environment, a grain size correction factor was applied to the bulk chemistry data for selected parameters showing elevated concentrations. Data were normalized for the fraction of the sediment <63 µm in diameter (i.e. the combined silt and clay fraction), on the assumption that all material coarser than this is inert, and that the metals concentrations are solely attributable to this fraction. Actual and grain-size corrected results for mercury, iron and copper are shown in Table 18.

The pattern of metals contamination in the sediment is considerably different following this correction. Although the grain-size corrected results for iron and copper again show elevated levels at the stations previously noted, distinct elevations in concentrations are now

Table 17. Corellation matrix for metals (coefficient (sample size) significance level).

	Silt & Clay %	Aluminum	Cadmium	Cobalt	Chromium	Copper	Iron	Mercury	Manganese	Nickel	Lead	Zinc
Silt & Clay %	1.0000 (42) 0.0000											
Aluminum	0.7477 (42) 0.0000	1.0000 (42) 0.0000										
Cadmium	0.5384 (42) 0.0002	0.3682 (42) 0.0164	1.0000 (42) 0.0000									
Cobalt	0.7315 (42) 0.0000	0.9636 (42) 0.0000	0.4755 (42) 0.0015	1.0000 (42) 0.0000								
Chromium	0.4442 (42) 0.0032	0.6936 (42) 0.0000	0.0625 (42) 0.6941	0.6837 (42) 0.0000	1.0000 (42) 0.0000							
Copper	0.8294 (42) 0.0000	0.7111 (42) 0.0000	0.7537 (42) 0.0000	0.7740 (42) 0.0000	0.4079 (42) 0.0073	1.0000 (42) 0.0000						
Iron	0.5481 (42) 0.0002	0.8430 (42) 0.0000	0.3262 (42) 0.0350	0.8726 (42) 0.0000	0.6506 (42) 0.0000	0.5803 (42) 0.0001	1.0000 (42) 0.0000					
Mercury	0.2342 (42) 0.1355	-0.1744 (42) 0.2694	0.2175 (42) 0.1666	-0.0819 (42) 0.6083	0.0292 (42) 0.8545	0.2102 (42) 0.1815	-0.1836 (42) 0.2446	1.0000 (42) 0.0000				
Manganese	0.6638 (42) 0.0000	0.6497 (42) 0.0000	0.4302 (42) 0.0045	0.6413 (42) 0.0000	0.2670 (42) 0.0874	0.7049 (42) 0.0000	0.5514 (42) 0.0002	-0.1796 (42) 0.2551	1.0000 (42) 0.0000			
Nickel	0.6688 (42) 0.0000	0.8529 (42) 0.0000	0.4057 (42) 0.0070	0.9122 (42) 0.0000	0.8093 (42) 0.0000	0.7339 (42) 0.0000	0.7236 (42) 0.0000	0.1278 (42) 0.4198	0.5446 (42) 0.0002	1.0000 (42) 0.0000		
Lead	0.7034 (42) 0.0000	0.4814 (42) 0.0012	0.6007 (42) 0.0000	0.5675 (42) 0.0001	0.2611 (42) 0.0949	0.8417 (42) 0.0000	0.3349 (42) 0.0302	0.4523 (42) 0.0026	0.5953 (42) 0.0000	0.6414 (42) 0.0000	1.0000 (42) 0.0000	
Zinc	0.7921 (42) 0.0000	0.5498 (42) 0.0002	0.6288 (42) 0.0000	0.6461 (42) 0.0000	0.3958 (42) 0.0095	0.8692 (42) 0.0000	0.4344 (42) 0.0040	0.5748 (42) 0.0001	0.4919 (42) 0.0009	0.7132 (42) 0.0000	0.9227 (42) 0.0000	1.0000 (42) 0.0000

Table 18. Grain-size corrected sediment results for metals.

Station No.	Depth (m.)	Silt & Clay %	Aluminum (ug/g)	Corr. Aluminum	Cadmium (ug/g)	Corr. Cadmium	Cobalt (ug/g)	Corr. Cobalt	Chromium (ug/g)	Corr. Chromium	Copper (ug/g)	Corr. Copper
22	54.0	76.0	8700	11447	ND	ND	6.2	8.2	38	50	9.6	12.6
24	27.0	37.2	7700	20699	0.20	0.54	7.3	19.6	29	78	14.0	37.6
369	4.5	1.9	3900	205263	0.20	10.53	3.2	168.4	24	1263	1.3	68.4
372	33.0	70.7	6200	8769	ND	ND	4.9	6.9	35	50	13.0	18.4
378	57.0	63.6	7900	12421	ND	ND	6.0	9.4	42	66	21.0	33.0
379	44.0	24.7	7300	29555	ND	ND	6.2	25.1	48	194	12.0	48.6
382	4.5	16.0	5600	35000	0.20	1.25	4.9	30.6	38	238	5.2	32.5
383	2.5	41.2	1900	4612	0.20	0.49	4.4	10.7	33	80	22.0	53.4
384	32.0	79.8	9600	12030	0.61	0.76	7.5	9.4	41	51	36.0	45.1
385	60.0	44.9	7000	15590	ND	ND	5.6	12.5	46	102	12.0	26.7
387	76.0	86.8	8800	10138	0.32	0.37	7.0	8.1	47	54	31.0	35.7
388	32.0	8.7	5400	62069	ND	ND	4.7	54.0	43	494	3.2	36.8
389	4.0	11.1	5000	45045	ND	ND	4.0	36.0	28	252	3.1	27.9
390	4.0	3.5	5200	148571	ND	ND	4.4	125.7	35	1000	3.4	97.1
391	2.2	1.5	6000	400000	ND	ND	4.6	306.7	33	2200	3.2	213.3
393	8.5	5.5	6000	109091	ND	ND	4.8	87.3	48	873	3.9	70.9
394	6.0	1.8	5600	311111	ND	ND	4.5	250.0	36	2000	3.5	194.4
395	2.2	3.3	5300	160606	ND	ND	4.5	136.4	29	879	2.8	84.8
397	108.0	89.2	10000	11211	0.36	0.40	7.5	8.4	47	53	34.0	38.1
398	72.0	76.1	8200	10775	0.61	0.80	6.8	8.9	39	51	25.0	32.9
400	43.0	12.7	6700	52756	ND	ND	5.6	44.1	45	354	6.4	50.4
402	16.0	3.6	5400	150000	ND	ND	4.5	125.0	41	1139	3.0	83.3
406	65.5	78.6	9100	11578	0.45	0.57	7.0	8.9	36	46	30.0	38.2
411	89.0	93.6	12000	12821	0.66	0.71	8.8	9.4	38	41	46.0	49.1
413	11.5	5.7	4300	75439	ND	ND	4.1	71.9	38	667	4.1	71.9
418	57.8	90.7	16000	17641	0.51	0.56	12.0	13.2	50	55	62.0	68.4
422	115.0	98.3	15000	15259	0.41	0.42	10.0	10.2	46	47	51.0	51.9
428	91.0	95.0	11000	11579	0.23	0.24	7.3	7.7	38	40	37.0	38.9
433	64.0	74.7	9500	12718	ND	ND	6.7	9.0	44	59	21.0	28.1
434	27.0	100.0	19000	19000	ND	ND	11.0	11.0	57	57	23.0	23.0
435	92.0	81.2	12000	14778	ND	ND	8.5	10.5	51	63	18.0	22.2
436	75.0	95.7	18000	18809	0.47	0.49	14.0	14.6	52	54	49.0	51.2
437	85.0	95.5	11000	11518	0.23	0.24	7.0	7.3	38	40	37.0	38.7
438	20.0	2.0	6800	340000	ND	ND	6.0	300.0	48	2400	11.0	550.0
590	9.0	5.7	5100	89474	ND	ND	4.1	71.9	36	632	2.6	45.6
591	22.5	50.5	6100	12079	0.20	0.40	5.2	10.3	31	61	5.1	10.1
592	43.5	79.8	8600	10777	0.20	0.25	6.3	7.9	41	51	29.0	36.3
593	55.0	100.0	21000	21000	ND	ND	13.0	13.0	58	58	24.0	24.0
594	16.0	88.4	8300	9389	0.20	0.23	5.8	6.6	39	44	26.0	29.4
1148	5.0	78.6	7000	8906	0.20	0.25	5.5	7.0	40	51	17.0	21.6
1149	35.0	56.2	7200	12811	0.20	0.36	5.6	10.0	44	78	16.0	28.5
1159	17.0	52.7	7200	13662	0.20	0.38	6.1	11.6	46	87	15.0	28.5

continued . . .

Table 18. Grain-size corrected sediment results for metals (concluded).

Station No.	Depth (m.)	Silt & Clay %	Iron (ug/g)	Corr. Iron	Mercury (ug/g)	Corr. Mercury	Manganese (ug/g)	Corr. Manganese	Nickel (ug/g)	Corr. Nickel	Lead (ug/g)	Corr. Lead	Zinc (ug/g)	Corr. Zinc
22	54.0	76.0	13000	17105	0.07	0.09	980	1289	16.0	21.1	6.8	8.9	25	33
24	27.0	37.2	22000	59140	0.06	0.16	550	1478	12.0	32.3	6.3	16.9	36	97
369	4.5	1.9	10000	526316	0.02	1.05	130	6842	6.6	347.4	ND	ND	17	895
372	33.0	70.7	12000	16973	1.20	1.70	210	297	12.0	17.0	6.4	9.1	35	50
378	57.0	63.6	13000	20440	1.80	2.83	260	409	16.0	25.2	12.0	18.9	45	71
379	44.0	24.7	14000	56680	0.48	1.94	190	769	18.0	72.9	5.2	21.1	37	150
382	4.5	16.0	13000	81250	0.26	1.63	150	938	13.0	81.3	4.3	26.9	34	213
383	2.5	41.2	8300	20146	8.80	21.36	120	291	19.0	46.1	41.0	99.5	91	221
384	32.0	79.8	15000	18797	4.80	6.02	310	388	19.0	23.8	18.0	22.6	63	79
385	60.0	44.9	13000	28953	1.20	2.67	190	423	16.0	35.6	6.3	14.0	37	82
387	76.0	86.8	15000	17281	2.60	3.00	380	438	19.0	21.9	19.0	21.9	59	68
388	32.0	8.7	15000	172414	0.22	2.53	160	1839	14.0	160.9	7.5	86.2	21	241
389	4.0	11.1	12000	108108	0.08	0.72	190	1712	11.0	99.1	3.0	27.0	19	171
390	4.0	3.5	12000	342857	0.11	3.14	140	4000	12.0	342.9	ND	ND	17	486
391	2.2	1.5	11000	733333	0.08	5.33	130	8667	13.0	866.7	ND	ND	18	1200
393	8.5	5.5	17000	309091	0.08	1.45	180	3273	14.0	254.5	ND	ND	19	345
394	6.0	1.8	11000	611111	0.08	4.44	130	7222	13.0	722.2	ND	ND	18	1000
395	2.2	3.3	9200	278788	0.07	2.12	110	3333	12.0	363.6	ND	ND	13	394
397	108.0	89.2	15000	16816	3.40	3.81	470	527	20.0	22.4	22.0	24.7	64	72
398	72.0	76.1	14000	18397	1.40	1.84	380	499	17.0	22.3	15.0	19.7	49	64
400	43.0	12.7	12000	94488	0.10	0.79	180	1417	18.0	141.7	ND	ND	28	220
402	16.0	3.6	14000	388889	0.08	2.22	160	4444	13.0	361.1	ND	ND	17	472
406	65.5	78.6	14000	17812	0.62	0.79	380	483	17.0	21.6	12.0	15.3	45	57
411	89.0	93.6	17000	18162	0.80	0.85	1000	1068	19.0	20.3	23.0	24.6	62	66
413	11.5	5.7	13000	228070	0.02	0.35	150	2632	12.0	210.5	ND	ND	13	228
418	57.8	90.7	21000	23153	0.40	0.44	720	794	25.0	27.6	26.0	28.7	77	85
422	115.0	98.3	20000	20346	0.44	0.45	1500	1526	24.0	24.4	31.0	31.5	72	73
428	91.0	95.0	15000	15789	0.33	0.35	1100	1158	17.0	17.9	21.0	22.1	53	56
433	64.0	74.7	16000	21419	0.71	0.95	400	535	17.0	22.8	13.0	17.4	45	60
434	27.0	100.0	21000	21000	0.02	0.02	440	440	24.0	24.0	12.0	12.0	49	49
435	92.0	81.2	17000	20936	0.17	0.21	1000	1232	21.0	25.9	11.0	13.5	40	49
436	75.0	95.7	24000	25078	0.50	0.52	920	961	30.0	31.3	23.0	24.0	74	77
437	85.0	95.5	15000	15707	0.92	0.96	1100	1152	17.0	17.8	23.0	24.1	56	59
438	20.0	2.0	15000	750000	ND	ND	220	11000	20.0	1000.0	ND	ND	20	1000
590	9.0	5.7	13000	228070	0.07	1.23	140	2456	12.0	210.5	ND	ND	14	246
591	22.5	50.5	14000	27723	0.27	0.53	180	356	13.0	25.7	3.1	6.1	24	48
592	43.5	79.8	14000	17544	4.40	5.51	260	326	16.0	20.1	14.0	17.5	54	68
593	55.0	100.0	23000	23000	ND	ND	460	460	28.0	28.0	15.0	15.0	53	53
594	16.0	88.4	14000	15837	1.80	2.04	220	249	15.0	17.0	12.0	13.6	55	62
1148	5.0	78.6	13000	16539	2.70	3.44	220	280	15.0	19.1	8.1	10.3	47	60
1149	35.0	56.2	15000	26690	5.10	9.07	200	356	16.0	28.5	5.7	10.1	45	80
1159	17.0	52.7	16000	30361	7.20	13.66	180	342	18.0	34.2	8.4	15.9	57	108

also evident around the main mill and WPCP outfalls at Stations #388, #389, #390, #391, #393, #394, #395, #402 and #590. The elevated concentrations at these stations suggests that the main mill and WPCP are also significant sources of these metals, but that they are not being deposited in sediments because of the coarse grain nature of the nearshore environment. Although a similar pattern is noted for mercury, the interpretation is restricted by the previously noted lack of correlation between concentrations and grain size.

3.3.3 Inorganic Parameters and Nutrients

The pH results ranged from 7.6 to 9.8, indicating more alkaline sediments. This may be attributable to the leaching of limestone found in the local Precambrian deposits.

Reducible sulphur compounds, including hydrogen sulphide, methyl mercaptan and various methyl sulphides, are commonly found in untreated whole mill effluents in sufficient concentrations to taint fish (Bonser et al. 1988). These compounds were detected at all stations where this parameter was analyzed. The highest concentrations were noted at Stations #378 (9700 µg/g), #384 (8300 µg/g) and #387 (8700 µg/g) in the area between Hawkins Island and the Peninsula.

Loss on ignition (LOI) values are a rough approximation of the amount of organic matter present in the sediments. The percentage LOI exceeded the OWDG of 6% at Stations #383, #594 and #1159 within the harbour (Table 16). The value was particularly high at Station #383 (66.2%), reflecting the deposition of organic matter (primarily wood fibres and bark) introduced by surface runoff and booming operations in this section of the harbour.

Total Organic Carbon (TOC) is another measure of the organic content of the soil. As with % LOI, one extremely elevated value was found at Station #383.

Solvent extractables are a measure of a group of compounds, primarily biological lipids and mineral hydrocarbons, that have a common solubility in an organic solvent. This is thus an imprecise measure of "oil and grease" compounds in the sediment. Solvent extractables exceeded the OWDG at six stations, five in the harbour and one adjacent to the WPCP outfall. The highest concentration 11820 µg/g was found at Station #382.

Phosphorous concentrations were generally low, reflecting the oligotrophic nature of Lake Superior. The OWDG was exceeded only at Station #422, in open Lake Superior.

3.3.4 Chlorophenols and Organochlorine Pesticides

Of the nine chlorophenol compounds analyzed, none were detected in the sediment samples. Five of the nine speciated phenolic compounds analyzed were detected at least once. Phenol, vanillin, homovanillic acid, guaiacol and acetovanillon were all detected at elevated levels at Stations #385 (between Hawkins Island and the Peninsula), #591 (west of Blondin Island) and #594 (in the north embayment of Peninsula Harbour). The presence of these compounds at this distance from the main mill outfall is surprising. As these compounds tend to degrade fairly rapidly (half-life ranging from a few days to several weeks (Bonser et al. 1988)), it is unlikely that they were deposited before the change in mill outfall to Lake Superior. The mill plume is known to travel northwest from the diffuser around the Peninsula into the mouth of Peninsula Harbour under appropriate wind conditions (Beak Consultants Limited 1986). This phenomenon, coupled with the depositional environments of these areas, may be responsible for the presence of these compounds at these stations.

Of the 21 organochlorine pesticides analyzed for in the sediments, nine were detected in at least one sample. Concentrations of pesticides were generally low. One high value for methoxychlor was recorded at Station #382 (150 ng/g). The infrequent detection and low concentrations of most organochlorine compounds suggest that there is no definable source of these compounds to this area.

PCB's were detected at 15 of the 35 stations (43%) where this parameter was analyzed. Concentrations exceeded the OWDG of 50 ng/g at 12 of these stations (Table 16). The geographic distribution of PCB concentrations in sediments is shown in Figure 15. Levels were particularly high (greater than 200 ng/g) at Stations #22 and #397 in open Lake Superior, at Station #382 in Jellicoe Cove and at Station #592 between Blondin and Hawkins islands. It is interesting to note that a concentration of 250 ng/g was recorded at Station #22 in 1973, illustrating the persistence of this group of compounds (Herzog and Chatterjee 1974).

High PCB values generally correspond to depositional areas of fine particle size (Figure 13). However, there is no overall significant correlation between grain size and

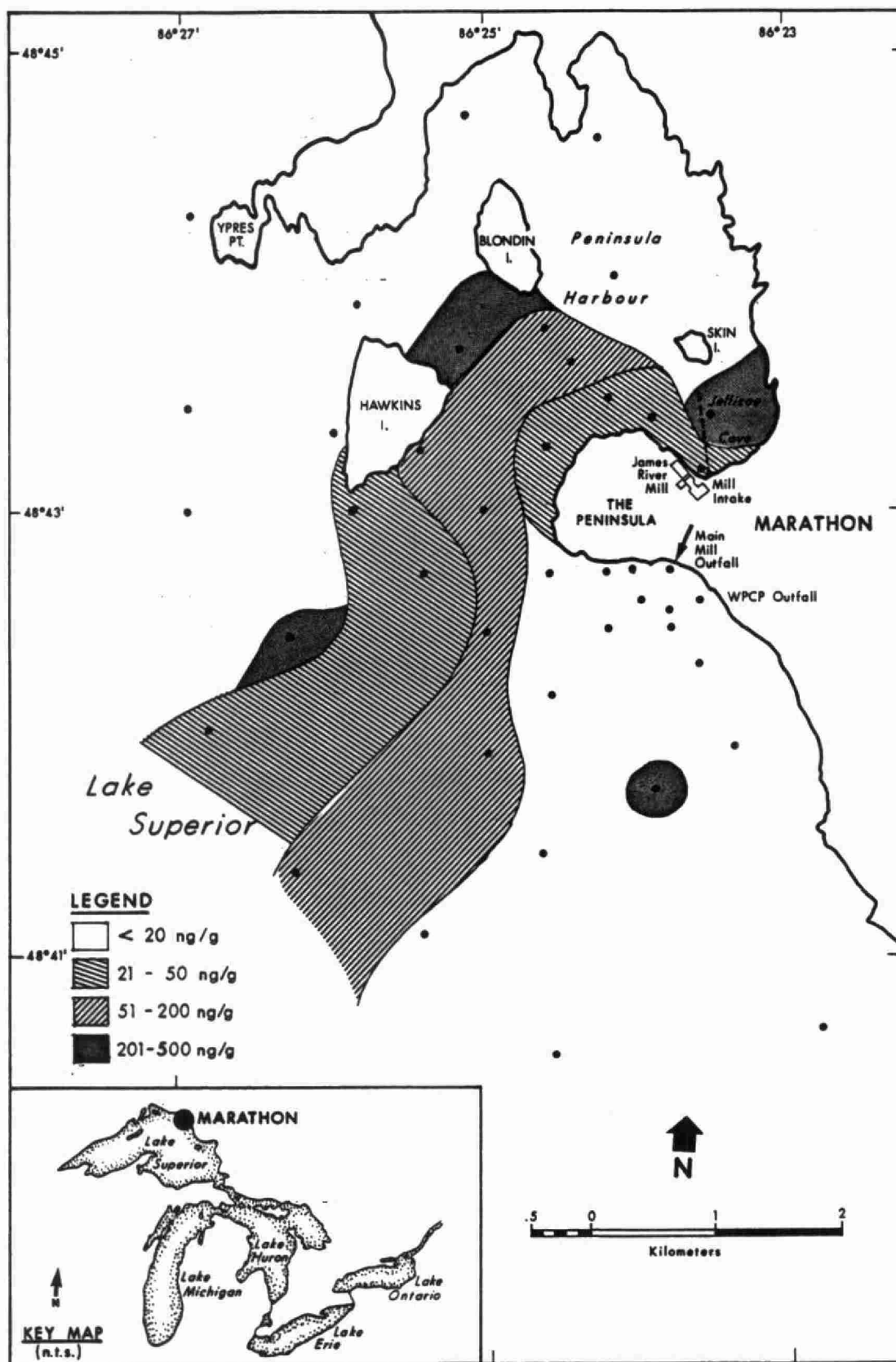


Figure 15. PCB concentrations in sediments collected in 1984.

concentration (correlation coefficient = -0.2809, $p = 0.3105$). A grain size correction was therefore not applied to this parameter.

4. SUMMARY AND CONCLUSIONS

4.1 EFFLUENT CHARACTERISTICS

4.1.1 WPCP Effluent

1. The effluent quality of the Marathon WPCP has improved significantly since the installation of secondary treatment. Total coliform counts in both 1984 and 1985 are substantially reduced from those reported in 1978, prior to the installation of secondary treatment. Bacterial contamination from the effluent no longer appears to be a problem. Significant decreases in apparent colour, nitrate and total phosphorous from May, 1984 to May 1985 indicate an improvement in the effluent quality. A significant increase in chloride concentrations probably reflects more intensive disinfection practices at the plant.
2. The effluent was well below the general OMOE effluent requirements for BOD₅ and total suspended solids of 25 mg/L for plants with secondary treatment, with levels less than 3.0 mg/L and less than 4.0 mg/L, respectively, in both 1984 and 1985. Total phosphorous concentrations slightly exceeded the GLWQA value for the Upper Great Lakes of 1.0 mg/L in both years, with mean values of 3.5 mg/L and 1.5 mg/L in 1984 and 1985 respectively. Given the oligotrophic nature of the receiving water, these levels are probably not of concern.
3. Significant decreases in Total Kjeldahl Nitrogen (TKN) and total phosphorous in the mill intake water may be related to similar significant decreases in nutrients in the WPCP effluent.

4.1.2 Pulp and Paper Mill Effluent

1. The mill was below the control order limit for discharge of suspended solids in both 1984 and 1985. Total dissolved solids and total solids decreased significantly during this time, although there was a concurrent increase in turbidity.
2. This mill slightly exceeded the control order limit for BOD₅ loadings on May 16, 1984, probably because of reduced production on this day. Samples collected on May 20, and monthly and yearly average loadings were within this limit. The mill

was within the regulatory limit for BOD₅ on all occasions in 1985. BOD₅ concentrations did not change significantly from 1984 to 1985. There was, however, a significant increase in chemical oxygen demand between the two years.

3. Sodium concentrations decreased significantly from a mean value of 380 mg/L in 1984 to a mean value of 321 mg/L in 1985. Metals concentrations were generally low, and remained constant between years, with the exception of a significant increase in lead. Although there was no statistically significant change in mercury, concentrations were reduced from a mean value of 1.59 mg/L in 1984 to 0.08 mg/L in 1985.
4. Total phosphorous concentrations were less than 0.5 mg/L in both years. Microbiological counts were, with the exception of low numbers of heterotrophic bacteria, below detection level. The low fecal coliform count indicates that *Klebsiella pneumoniae* contamination is not a problem with this mill.
5. Three resin acids (dehydroabietic acid, pimaric acid and isopimaric acid) decreased significantly from 1984 to 1985. This may be due to the use of hardwoods and softwoods as furnish in 1985, as opposed to solely softwoods in 1984. Three of the fatty acids (palmitic acid, stearic acid and linoleic acid) also decreased significantly.
6. Total reactive phenolics in the effluent were greater than 2000 µg/L in both years. Vanillin and 2,4,6-trichlorophenol also decreased significantly. Despite this apparent decrease in the concentration of toxic components, the mill effluent continues to be highly toxic to fish. In 1986, the rainbow trout 96 hour LC₅₀ was 12 - 15%. The high toxicity implies that the observed decrease in toxic components is a temporary phenomenon associated with hardwood runs.
7. The parameters exhibiting significant differences in concentration between years in the mill effluent and intake water are completely exclusive, indicating that the changes noted in the mill effluent quality are primarily attributable to process and treatment changes in the mill.

4.2 WATER QUALITY CHARACTERISTICS

4.2.1 Effluent Plume and Water Column Profiles

1. Plume tracking efforts were generally unsuccessful because of erratic wind conditions, verifying the variable nature of the plume size and configuration.
2. The depth profiles conducted at the stations within the harbour and in open Lake Superior showed relative uniformity of conductivity, water temperature and dissolved oxygen (1984 only) from the surface to the bottom. These results indicate a well-mixed water column. Stations near the mill outfall showed minor variations in conductivity and water temperature throughout the water column in both years. The profiles illustrated the difference between 1984 surface discharge and 1985 bottom discharge.
3. Most parameters exhibited a distinct dilution profile above the submerged diffuser outfall. Concentrations at the diffuser tended to decrease from the first to the last port. Differences in the profiles for total reactive phenolics at two different time periods in the same day again reflect the strong influence of wind speed and direction on the effluent plume and subsequent dilution.

4.2.2 Water Quality

1. Conductivity (25°C), total dissolved solids, total suspended solids, sodium, ammonia, BOD₅, COD and total reactive phenolics decreased significantly from 1984 to 1985. These parameters are associated with both the mill and WPCP effluents. These improvements may be attributed to improvement in effluent quality and increased dilution of the effluent resulting from the installation of the submerged diffuser discharge. However, the extent of improvement is difficult to assess because of the variability in plume configuration and extent.
2. Water temperature, turbidity, iron and nitrate increased significantly from 1984 to 1985.
3. Significant station differences were found for turbidity, sodium, chloride, BOD₅ and total reactive phenolics, indicating a definitive point source of these parameters.

4. Dissolved and suspended solids have decreased considerably from those recorded in previous surveys, and no longer appear to be a problem in the receiving water.
5. Mapping of sodium and total reactive phenolics concentrations on each sampling date further verifies both the variability of the plume and reduction in localized concentrations resulting from increased initial dilution of the effluent in 1985.
6. Metals concentrations in water samples were generally low, with some samples exceeding the PWQO's by a moderate amount. Compounds exceeding the objectives were: aluminum (1985 only - 1 station); cadmium (1984 - 1 station, 1985 - 4 stations); iron (1985 only - 2 stations); lead (1984 - 1 station; 1985 - 2 stations); mercury (1984 only - 1 station); and zinc (1984 - 1 station, 1985 - 7 stations). Although concentrations of total elemental mercury are generally below objectives, the concentrations of biologically available methylmercury are not known, and the full extent of mercury contamination cannot be assessed.
7. The concentrations of ammonia, total Kjeldahl nitrogen (TKN), nitrite and nitrate did not exceed any water quality objectives, and were generally similar to background levels. Total phosphorous exceeded the PWQO for avoidance of nuisance algal growth at one station in 1984 and at nine stations in 1985 (near the mill and WPCP outfalls). However, algal problems are unlikely, given the oligotrophic nature of Lake Superior.
8. Bacterial counts were considerably reduced from previous surveys, and well below PWQO's for recreational use. Bacterial contamination would appear to no longer be a receiving water impairment in Peninsula Harbour or open Lake Superior.
9. The high, localized biochemical and chemical oxygen demands associated with the waters near the mill outfall were not evident in 1985 after the instalment of the submerged diffuser outfall.
10. Dissolved oxygen concentrations in the study area are high (generally greater than 12 mg/L), indicating that the oxygen demand from the effluents does not appear to be depleting oxygen in the receiving water environment.

11. The PWQO's for dehydroabiatic acid and total resin acids were exceeded at one station below the mill and WPCP outfalls in 1985 only. Fatty acids were also only detected at this station.
12. Most volatile organohalide compounds analyzed were not detected. Chloroform, carbon tetrachloride, trihalomethanes and 2,3,6-trichlorotoluene (1985 only) were detected at a limited number of stations.
13. Of the organochlorine pesticides, only α -BHC, γ -BHC (lindane) and aldrin were detected at low levels. These compounds are regularly detected at low concentrations throughout the Great Lake basin.
14. Although the PWQO for total reactive phenolics was exceeded frequently in both years, there have been no recent reports of fish tainting in this area.
15. No chlorophenolic compounds were detected in receiving waters. Of the speciated phenolics, only phenol, homovanillic acid and acetovanillon were detected in 1985. Vanillin and guaiacol were detected in both years, but more frequently in 1985. The increased detection in 1985 is probably due to the change in method sensitivity and reporting units for these compounds.

4.3 SEDIMENT QUALITY

1. The dynamic nearshore environment was characterized by sandy, coarse sediment. The finer sediments were found in the deeper depositional environments offshore.
2. Chromium and iron concentrations were above the OWDG's in most samples, while copper and iron concentrations only occasionally exceeded the guidelines.
3. Mercury concentrations exceeded the OWDG at 52% of the stations, with the highest concentration of 8.80 $\mu\text{g/g}$ found near the site of the former chlor-alkali plant in Jellicoe Cove. High concentrations were also found in the mouth of the harbour. Mercury concentrations were considerably reduced from those found in previous surveys. This reduction may be the result of the deposition of cleaner sediment over the contaminated locations and/or migration into deeper depositional areas.

4. All metals except chromium and mercury are positively correlated with particle size (combined silt and clay fraction), implying that concentrations at a given station are a function of both proximity to the source and depositional environment. Grain-size corrected results for iron and copper suggest that the mill and WPCP may be significant sources of these metals, but that they are not being deposited here because of the dynamic nature of the near-shore environment.
5. The organic content of the sediments, as measured by % LOI and TOC, is particularly high in Peninsula Harbour. This reflects the deposition of wood fibres and bark introduced by booming operations and surface runoff. Three stations exceeded the OWDG for % LOI in the harbour, with particularly high values in Jellicoe Cove.
6. Phosphorous concentration were generally low, with the OWDG being exceeded at only one station in open Lake Superior.
7. None of the chlorophenolic compounds analyzed were detected. The five speciated phenolic compounds detected in the water column were also found in the sediments in the harbour area.
8. Only nine of the 21 organochlorine pesticides analyzed for were detected in at least one sediment sample.
9. PCB's were detected at 15 of the 35 stations where this compound was analyzed. Concentrations exceeded the OWDG at 12 of these stations. The persistence of this group of compounds is illustrated by the comparable levels (above 200 ng/g) found at the same station in Lake Superior in 1984 and 1973.

5. RECOMMENDATIONS

1. Although sediment mercury concentrations are still above the open-water disposal guidelines, contamination is considerably reduced at the site of the former chlor-alkali discharge. This may be due to the deposition of cleaner sediments over the contaminated areas and/or migration and dispersion of the mercury from the original source into deeper depositional areas. Further assessment of sediment mercury should be conducted in depositional areas to determine the full areal extent of the contamination. Sediment cores should be collected in the areas of maximum concentration in Jellicoe Cove to determine the historical extent of mercury deposition. In addition, methylated mercury analyses should be done on both water and sediment samples from these areas to assess the bioavailability of the mercury to aquatic fauna.
2. PCB sediment contamination should be monitored on a regular basis to determine if the concentrations and areal extent of the contamination are changing over time. PCB concentrations should also be determined concurrently in the mill and WPCP effluent solids to determine if the contamination is due to current as well as historical deposition.
3. Based on the results of the surveys recommended in #1 and #2, options for remediation of contaminated sediments should be developed
4. As the quality of the effluent discharges and receiving water have improved since previous benthic invertebrate surveys, these surveys should be repeated to determine the effects of these changes on the macroinvertebrate populations and community structure.
5. The bioavailability and toxicity of contaminants in the sediment and water column should be determined through biomonitoring assessment procedures such as caged mussel and leech exposures, and sediment bioassays.
6. In view of recent concerns on organochlorine discharges from kraft pulp mills, further assessment should be made of these compounds and/or groups of compounds in the effluent, water, sediment and biota. Investigations into the

presence of chlorinated dibenzo-p-dioxins and dibenzofurans are of particular concern.

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Remedial Action Plan Plan d'Assainissement

Canada Ontario 

Canada-Ontario Agreement Respecting Great Lakes Water Quality
L'Accord Canada-Ontario relatif à la qualité de l'eau dans les Grand Lacs